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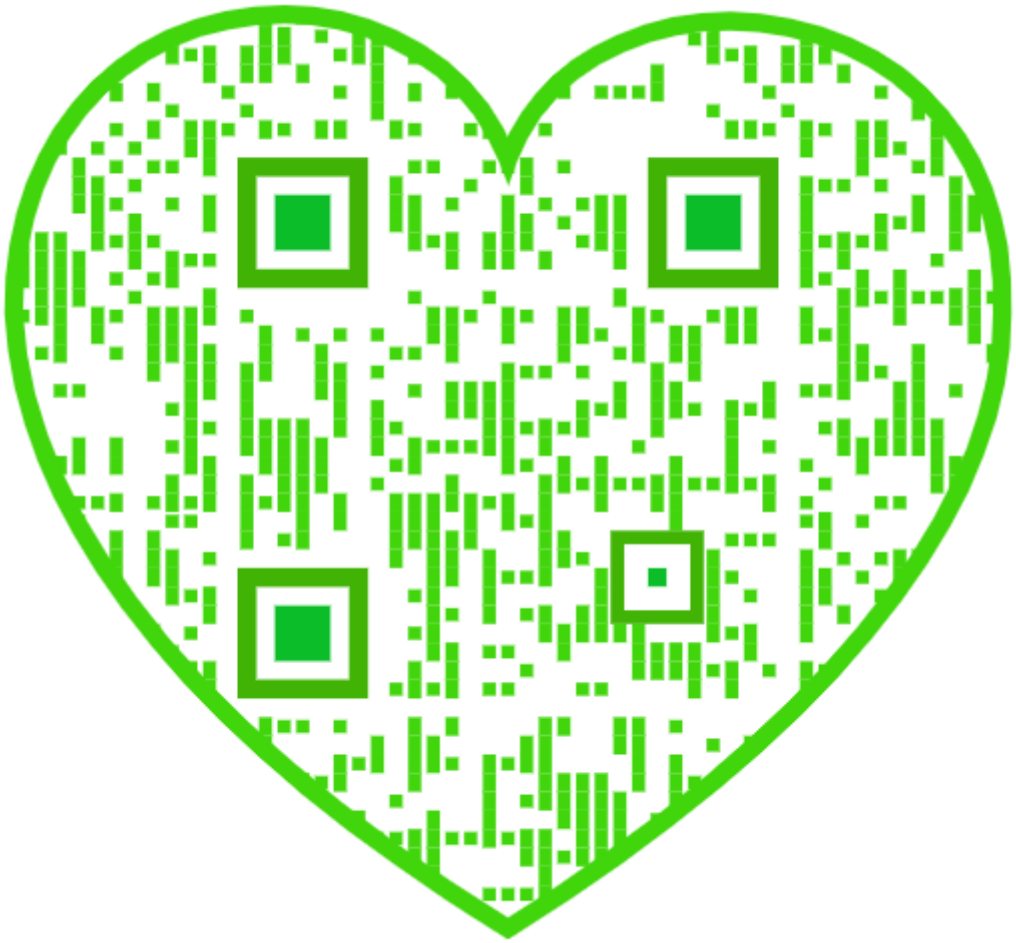

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CHAPTER I

NITRIC ESTERS—GENERAL OUTLINE

STRUCTURE

ESTERS of nitric acid are characterized by the following atomic grouping:

$$—C—O—NO_2$$

that is by the presence of the nitroxy group. The nitro group in nitric esters is attached to a carbon atom by means of an oxygen atom, i.e. they are O-nitro compounds. This is confirmed by the fact that nitric esters undergo hydrolysis, and that as the result of reduction of the nitro group, an alcohol is obtained:

$$R—ONO_2 \xrightarrow{[H]} R—OH + NH_3$$

This reaction shows the essential difference between nitric esters and nitro compounds: the latter form amines under these conditions.

The structure of the nitro group present in nitric esters is the same as that in nitro compounds.

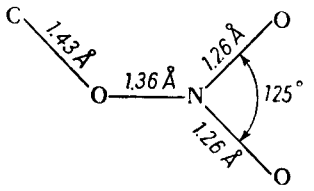
The reactivity of nitric acid esters and in particular the complicated chemical composition of the products formed by their hydrolysis led some investigators [1, 37] to express the view that nitric esters may have the structure of peroxy-compounds (I):

$$R—O—O—NO$$
$$\text{I}$$

However there exists no evidence for this. Moreover, investigation of the absorption spectra of nitric acid, nitrous acid and aliphatic nitro compounds indicates that the peroxide structure hypothesis is incorrect, because nitric acid esters behave as compounds having the normal ester structure (II) (Crigee and Schnorrenberg [1a], Matsushima [1b]):

$$R—O—NO_2$$
$$\text{II}$$

X-Ray investigations, electron diffraction, Raman and infra-red spectra, and dipole moment measurements of nitric esters also support the idea of a symmetrical structure for the nitrate group (in spite of certain discrepancies obtained by different authors):



The bond distances and angles approximate to these found in nitro compounds. The most accurate figures were determined with methyl nitrate [109].

PHYSICAL PROPERTIES

Esters formed by combination of nitric acid with lower alcohols are liquids, the boiling points of which are slightly higher than the boiling temperatures of the respective alcohols, but significantly higher than the boiling points of esters of nitrous acid. C-nitro compounds are characterized by higher boiling temperatures than the corresponding nitric acid esters (Table 1).

TABLE 1
BOILING POINTS OF ALCOHOLS, ESTERS AND NITRO COMPOUNDS, °C

Alkyl	Alcohol	Nitric ester	Nitrous ester	Nitro compound
Methyl	65	65	−12	101
Ethyl	78	88	17	114
n-Propyl	96	111	47	131
Isopropyl	82	102	45	120
n-Butyl	117	136	75	151

The small differences between the boiling points of the alcohols and their nitric acid esters can be explained by the fact that the alcohols are highly associated liquids (mainly through hydrogen bonds). Due to this molecular association the viscosity of the alcohols is also higher than the viscosity of their nitric esters. On the other hand the presence of a semi-polar bond in the nitro group of nitric esters is responsible for their relatively high vapour pressure, as in nitro compounds, causing them to be more volatile than the corresponding alcohols.

De Kreuk [2] made the first systematic study of the various physical constants of nitric esters, i.e.: dielectric constant (ε_{20}), refractive index (n_{∞}^{20}), density (d_4^{20}) and viscosity (η_{20}), (Table 2). Figures for tribromohydrin and triacetin are given for comparison.

According to de Kreuk the difference between the viscosity values of similar compounds (e.g. 1,3- and 1,2-propanediol dinitrates, 1,3- and 2,3-butanediol dinitrates) may be attributed to rotational isomerism. Free rotation makes possible the formation of *trans* isomers which according to this author should possess a higher viscosity. This would explain the relatively high viscosities of 1,3-propanediol and 1,3-butanediol dinitrates.

Boileau and Thomas [3] have determined certain physical constants for nitroglycerine and a few glycol dinitrates of practical importance (Table 3).

TABLE 2

Substance	ε_{20}	n_{∞}^{20}	d_4^{20}	η_{20} (cP)
n-Butyl nitrate	13.10	1.39526	1.0156	0.87
Ethylene glycol dinitrate	28.26	1.43235	1.4918	4.61
1,3-Propanediol dinitrate	18.97	1.43476	1.3952	5.8
1,2-Propanediol dinitrate	26.80	1.42720	1.3774	4.65
1,3-Butanediol dinitrate	18.85	1.43259	1.3167	6.00
2,3-Butanediol dinitrate	28.84	1.42754	1.3061	4.7
Nitroglycerine	19.25	1.45731	1.5931	37.8
3-Chloro-1,2-propanediol dinitrate	17.50	1.45850	1.5323	12.4
1,3-Dichloro-2-propanediol nitrate	13.28	1.46032	1.4630	4.8
Tribromohydrin	6.45	1.56190	2.4360	
Triacetin	7.19	1.41929	1.1596	

TABLE 3

Ester	Viscosity, η		Density d_{16}^{16}	Refractive index $n_D^{21.2°}$
	temp., °C	P		
Nitroglycerine	5.1	1.033	1.5985	1.4725
	20.0	0.352		
	55.0	0.0875		
Dinitroglycol	7.1	0.0633	1.4918	1.4463
	20.0	0.0423		
	54.4	0.0198		
1,3-Propanediol dinitrate	6.3	0.0940	1.4053	1.4483
	20.2	0.0550		
	54.2	0.0275		
Diethylene glycol dinitrate	5.3	0.133	1.3890	1.4505
	20.4	0.0727		
	54.4	0.0337		
Triethylene glycol dinitrate	6.0	0.257	1.3291	1.4542
	20.3	0.119		
	54.2	0.015		

Dipole moments

Dipole moments of alkyl nitrates were determined by Cowley and Partington [4]. They found the value $\mu = 2.73$ D for methyl nitrate. The values of μ in the instance of longer chain alkyls do not differ essentially from this figure.

De Kreuk [2] also calculated dipole moments using his observed values of ε and n_{∞}^{20}. His figures are given in Table 4.

TABLE 4

Substance	Dipole moment, μ (D)	
	Pure substance	In benzene solution
n-Butyl nitrate	2.90	2.98
Ethylene glycol dinitrate	4.00	3.28
1,3-Propanediol dinitrate	3.50	3.14
1,2-Propanediol dinitrate	4.24	3.72
1,3-Butanediol dinitrate	3.74	3.45
2,3-Butanediol dinitrate	4.72	4.12
Nitroglycerine	3.82	3.16
3-Chloro-1,2-propanediol dinitrate	3.46	3.05
1,3-Dichloro-2-propanediol nitrate	2.86	2.59
Tribromohydrin	1.63	1.58
Triacetin	2.50	2.58

The difference between the dipole moments of the pure substance and their value in benzene solution is (according to de Kreuk) due to the possible formation of a certain amount of *trans* rotation isomer in benzene. High values for pure 1,2-propanediol dinitrate and 2,3-butanediol dinitrate are due to the presence of a high proportion of the *cis* form in the pure liquids.

Although the conclusion of de Kreuk on the influence of rotational isomerism on dipole moments is correct, his quantitative estimation of the proportion of isomers is not convincing as it was based on some assumptions.

Mortimer, Spedding and Springall [5] examined the dipole moments of pentaerythritol tetranitrate and also concluded that the existence of rotational isomers was possible.

Recently T. Urbański and Witanowski [6] have suggested, on the basis of infrared absorption spectra, that rotational isomers are present in nitrates of the general formula

$$\begin{array}{l} R-CHX-CH-R' \\ \qquad\qquad\quad | \\ \qquad\qquad ONO_2 \end{array}$$

when X is relatively large, e.g. X = ONO_2, NO_2, CN, I, Br, Cl (see pp. 6 and 45).

Spectroscopy

The O-nitro group (the nitroxy group) gives an absorption band of about 270 mμ, in the ultra-violet region, i.e. a band similar to that of the C-nitro group. A relatively small amount of work has been done on the ultra-violet absorption spectra of nitric acid esters but it has been established that in esters containing no other chromophoric groups absorption is extremely low (ε = 10–20) even lower than in case of aliphatic nitro compounds.

Data published by Masaki [7] and by R.N. Jones and Thorn [8] are collected below in Table 5.

TABLE 5

Compound	Solvent	Maximum absorption		Author
		wavelength mμ	extinction ε	
$C_2H_5ONO_2$		270	10	Masaki
$C_2H_5ONO_2$	Ethanol	265	14.8	Jones and Thorn
α-Methyl-glucose 6-nitrate	Water	265	19.0	Jones and Thorn
2,3,4-Trimethyl-methyl-α-glucose 6-nitrate	Ethanol	265	21.4	Jones and Thorn

A few ultra-violet spectra of nitric esters were also given by Dalmon and Bellin [9].

As early as 1929 Plyler and Steele [10] began an investigation of the infra-red spectra of nitric esters in the range methyl to n-butyl nitrates. Dadieu, Jele and Kohlrausch [11] studied the Raman spectra of nitric esters as well as inorganic nitrates, and aliphatic and aromatic nitro compounds.

The Raman spectra of nitric esters have received relatively less attention for two reasons:

(a) their tendency to decompose under irradiation with ultra-violet light,

(b) the greater danger involved in using the relatively large samples needed.

Nevertheless a number of important researches were carried out prior to 1945, i.e. at the time when the infra-red technique was not fully perfected, among which the experiments of Médard [12], Chédin [13], Lecomte and Mathieu [14], Wittek [15], Nielsen and Smith [16] are worthy of note.

Further experiments on the infra-red spectra of alkyl nitrates were carried out by: Kettering and Sleater [17], Lenormant and Clement [18], Brand and Cawthon [19], Kornblum, Ungnade and Smiley [20], Carrington [21], Guthrie and Spedding [22].

Kumler [23], McCallum and Emmons [24] examined the infra-red spectra of nitric esters of hydroxyacids.

Namba, Yamashita and Tanaka [25] investigated the infra-red spectra of penta-, dipenta- and tripentaerythritol nitrates.

An extensive study was carried out by Brown [26] who examined over twenty esters of nitric acid and found the characteristic stretching frequencies of the NO_2 ester group:

asymmetric	1639 ± 13 cm^{-1}
symmetric	1279 ± 7 cm^{-1}

Bellamy [27] examined a number of nitric esters, among them ethylene glycol dinitrate and pentaerythritol tetranitrate and found the stretching frequencies to be 1650–1610 and 1300–1250 cm^{-1} respectively.

This is well in line with the Raman spectrum which, according to various authors,

gives two frequencies near 1640 and 1290 cm^{-1} characterizing vibrations of the NO_2 group. Similar figures were given for Raman spectra by Nielsen and Smith [16].

Among more common nitric esters, nitrocellulose was examined by Ellis and Bath [28] and Nikitin [29] (p. 287). Nitroglycerine and diethylene glycol dinitrate were examined for the first time by Pinchas [30]. Pristera [31] investigated a number of nitrates used as propellant ingredients, such as nitroglycerine, metriol trinitrate, diethylene glycol dinitrate (DEGN) and triethylene glycol dinitrate (TEGN). According to Pristera all of them give two bands with frequencies near 1667 cm^{-1} (6 μ) and 1282 cm^{-1} (7.8 μ). The particular compounds vary in details with regard to the shape of the absorption curves. Thus, the tip of the symmetric stretching band of diethylene glycol dinitrate (*ca.* 1639 cm^{-1}) has a shoulder, whereas that of triethylene glycol dinitrate has not. The 1282 cm^{-1} band of nitroglycerine has a strong shoulder which does not exist in the spectra of other nitrates. The shoulders are most likely due to rotational isomerism [6].

On the basis of the results obtained with more than 40 nitric esters, T. Urbański and Witanowski [6] have found the following frequencies of vibrations characteristic to nitric esters:

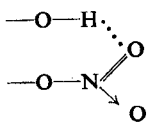
asymmetric stretching ν_{as} (NO_2)	1675–1621 cm^{-1}
symmetric stretching ν_s (NO_2)	1301–1268 cm^{-1}
stretching ν (C—O)	1100–950 cm^{-1}
stretching ν (O—N)	880–815 cm^{-1}
wagging γ_w (NO_2)	760–737 cm^{-1}
bending δ (NO_2)	710–640 cm^{-1}
rocking γ_r (NO_2)	*ca.* 580 cm^{-1}

It was found that asymmetric NO_2 vibrations are readily subject to a change in frequency when R in the molecule $R—ONO_2$ is changed. A positive and negative induction effect of R respectively lowers and raises the frequency of ν_{as} (NO_2). This fact makes it possible to distinguish between primary, secondary and tertiary alkyl nitrates.

Both the asymmetric and symmetric NO_2 vibration bands are shifted towards higher frequencies when the ONO_2 group is approaching another bulky group. This helps in recognizing the rotational isomerism mentioned above (p. 4). As a result of the presence of rotational isomers both the stretching vibrations of the NO_2 group are split into two (and in some instances more) maxima differing appreciably:

asymmetric by 1–25 cm^{-1}
symmetric by 10–35 cm^{-1}

No internal hydrogen bond was detected between OH and ONO_2 groups



indeed it seems that ONO_2 inhibits the formation of an intermolecular hydrogen bond between itself and OH groups.

HYDROLYSIS OF NITRIC ESTERS

Nitric esters of monovalent and polyvalent alcohols are hydrolysed by comparatively mild reagents in alkaline or acid media and with slightly more difficulty in a neutral medium. Theoretically, this process might be expressed by the following equation:

$$RONO_2 + H_2O \longrightarrow ROH + HNO_3 \quad (1)$$

However, the alcohol and acid formed during the hydrolysis of nitric esters are accompanied by a range of other compounds such as aldehydes, ketones, hydroxycarboxylic acids, unsaturated hydrocarbons, nitrous acid, etc. (e.g. reference [107]).

In certain cases the hydrolysis process does not result in the formation of the initial alcohol at all, but a series of other compounds is obtained, by a reaction mechanism which is often unknown. As an example, the hydrolytic reaction of nitroglycerine performed in an aqueous or alcoholic solution of sodium or potassium hydroxide can be quoted. Oxidation and reduction processes take place simultaneously to form organic acids as well as nitrates and nitrites. After Hay [32] the course of the reaction can be summarized by the eqn. (2):

$$C_3H_5(ONO_2)_3 + 5KOH \longrightarrow KNO_3 + 2KNO_2 + CH_3COOK + HCOOK + 3H_2O \quad (2)$$

This equation does not present a full picture of the chemical changes that occur, before Vignon and Bay [33], Silberrad and Farmer [34] and Berl and Delpy [35] identified the presence of aldehyde resins, oxalic acid and ammonia among the products of hydrolysis performed under similar conditions.

The absence of glycerine among the products of hydrolysis in alkaline medium was also confirmed by Carlson [36].

According to Klason and Carlson [37] glycerol is formed, however, when nitroglycerine is hydrolysed in alkaline media containing readily oxidizable substances, as for instance phenyl mercaptan.

Much experimental work has been carried out in seeking an explanation of the mechanism of the hydrolysis process of nitric esters but a relatively satisfactory theoretical explanation of the phenomenon has been found only recently.

Klason and Carlson were of the opinion that the formation of nitrous acid takes place owing to the peroxy structure of nitric esters, as these, under the influence of a hydrolysing agent, would change their structure and be transformed into peroxy compounds. Simultaneously nitrous acid would be formed:

$$ROONO + H_2O \longrightarrow ROOH + HNO_2 \quad (3)$$

Now since the chemical structure of nitric esters has already been established, this hypothesis has been abandoned.

However, Matsushima [1b] suggested that peroxides may be formed in the course of hydrolysis of nitric esters (4) as transition products prior to the formation of aldehydes (5):

$$RCH_2ONO_2 + H_2O \longrightarrow RCH_2OOH + HNO_3 \quad (4)$$

$$RCH_2OOH \longrightarrow RCHO + H_2O \quad (5)$$

According to Farmer [38] the first stage of hydrolysis proceeds in accordance with the eqn. (1) (p. 7). Afterwards, the products react with one another to form nitrous acid or nitrites and the series of compounds ennumerated above. Farmer's hypothesis seems unsatisfactory when hydrolysis of nitric esters is carried out in a neutral medium since, for example, if ethyl alcohol is treated with an aqueous solution of potassium nitrate no oxidation of the ethyl alcohol occurs even if the mixture of compounds is boiled.

An instance of the production of olefins has been detected by Lucas and Hammett [39] as the result of hydrolysing the nitric ester of tertiary butyl alcohol. In this case, in addition to the corresponding alcohol a certain quantity of isobutylene is also formed, as shown by eqn. (7):

$$C_4H_9ONO_2 + 2H_2O \longrightarrow C_4H_9OH + H_3O^{\oplus} + NO_3^{\ominus} \quad (6)$$

$$C_4H_9ONO_2 + H_2O \longrightarrow C_4H_8 + H_3O^{\oplus} + NO_3^{\ominus} \quad (7)$$

In experiments with benzyl nitrate the same workers have established that during the hydrolysis of this ester a certain quantity of benzaldehyde is obtained together with benzyl alcohol:

$$C_6H_5CH_2ONO_2 + 2H_2O \longrightarrow C_6H_5CH_2OH + H_3O^{\oplus} + NO_3^{\ominus} \quad (8)$$

$$C_6H_5CH_2ONO_2 \xrightarrow{H_2O} C_6H_5CHO + HNO_2 \quad (9)$$

Experimental data collected by Baker and Easty [40] during a study of the hydroysis of nitric esters has led them to conclude that this reaction can proceed in three directions as shown in the following equations:

$$RCH_2CH_2ONO_2 + Y^{\ominus} \longrightarrow RCH_2CH_2Y + NO_3^{\ominus} \quad (10)$$

$$RCH_2CH_2ONO_2 + Y^{\ominus} \longrightarrow RCH{=}CH_2 + NO_3^{\ominus} + HY \quad (11)$$

$$RCH_2CH_2ONO_2 + Y^{\ominus} \longrightarrow RCH_2CHO + NO_2^{\ominus} + HY \quad (12)$$

Y being a hydrolysing agent.

In the first case (10) a reaction of nucleophilic substitution takes place; the second equation (11) indicates that a hydrogen atom in the β-position can be removed; similarly the removal of an α-hydrogen atom is postulated in eqn. (12).

The experiments mentioned above were performed in aqueous solutions of alcohol containing aliphatic mononitrates. The hypothesis of Baker and Easty is supported by the established fact that methyl nitrate fails to react according to eqn. (11) and that tertiary butyl nitrate is unable to decompose in the way suggested by reaction (12). It is also noteworthy that methyl nitrate reacts according to (12)

only in an insignificant degree and that only about 4% of ethyl nitrate takes part in reactions (11) and (12) whereas all the remainder of this compound hydrolyses in accordance with eqn. (10). The rates of the reactions (10), (11) and (12) correspond to ratios of 70:7:1.

Reductive hydrolysis of n-butyl nitrate in an aqueous solution of ethyl alcohol in the presence of sodium hydrosulphide or ammonium hydrosulphide has been carried out by Merrow, Cristol and van Dolah [41]. This is a complicated chemical reaction. As the result of hydrolysing the nitrate in the presence of sodium hydrosulphide (the alkalinity of the solution corresponds to pH 10–11) 93% of nitrite ions and 7% of ammonia are obtained from the ester group nitrogen. When ammonium hydrosulphide is used, the nitrite ions initially produced rise to a maximum concentration and then fall to zero owing to the reducing action of the ammonium hydrosulphide. The reduction process takes place more effectively when the pH is above 10.

The reactions can be represented by the eqns. (13) and (14):

$$C_4H_9ONO_2 + 2NaHS \longrightarrow C_4H_9OH + NaNO_2 + NaHS_2 \tag{13}$$

$$C_4H_9ONO_2 + 4NH_4HS + 3H_2O \longrightarrow C_4H_9OH + 4S + 4NH_4OH \tag{14}$$

Sodium hydrosulphide hydrolysis was commonly applied on an industrial scale in order to regenerate cellulose from nitrocellulose fibre. For this chemical process the following type of reaction can be suggested:

$$C_6H_8O_3(ONO_2)_2 + 2NaHS \longrightarrow C_6H_{10}O_5 + 2NaNO_2 + 2S \tag{15}$$

$$2NaHS + 2S \longrightarrow Na_2S_3 + H_2S \tag{16}$$

Nadai [42] proposed a slightly different mechanism for the hydrolysis of nitrocellulose by hydrosulphides:

$$RONO_2 + HO^{\ominus} \longrightarrow ROH + NO_3^{\ominus} \tag{17}$$

$$NO_3^{\ominus} + 2HS^{\ominus} \longrightarrow NO_2^{\ominus} + HS_2^{\ominus} + HO^{\ominus} \tag{18}$$

Both the hydrolysis of nitrocellulose by means of hydroxides and the hydrolytic decomposition of butyl nitrate, as established by Merrow *et al.*, proceeds very slowly. For example, if a 0.1 *M* solution of butyl nitrate is hydrolysed at a temperature of 26.9°C by the action of 0.2 *M* sodium hydroxide dissolved in 60% ethanol, then after 16 days, only about 10% has entered into the reaction. With the addition of hydrosulphide, the process is completed within a period of 4 hr.

The above mentioned authors also established that the nitrate ion (in contrast with the nitrite ion) slowly undergoes reduction in the presence of sodium hydrosulphide. This leads to the conclusion that the nitrite ion formed during the hydrolysis of nitric esters cannot be produced by the reduction of a nitrate ion. Hence if the nitrite ion is formed direct during the hydrolysis of nitric esters, then it could only be produced by breaking the linkage between the oxygen and nitrogen atoms.

Since in numerous cases of hydrolysis of nitric esters the presence of a large amount of nitrate ion has been established, which could be liberated only by rupture of the C—O bond, the factors that influence the direction of this process should be discussed. Several investigations have thrown light on this problem, which is more complicated than with carboxylic esters, since during the hydrolysis of the latter compounds whether in acid or in alkaline medium only rupture of the ester bond can take place. This has been established in various ways including the use of water containing an ^{18}O-isotope. In general the hydrolysis of carboxylic esters can be defined by the equation:

$$R-\overset{\overset{O}{\|}}{C}-O-R' + H-{}^{18}O-H \longrightarrow R-\overset{\overset{O}{\|}}{C}-{}^{18}O-H + R'-OH \qquad (19)$$

This reaction scheme has been confirmed by the hydrolysis of esters containing an optically active alcohol: no racemization of the alcohol occurs during the reaction.

In the investigation with n-butyl nitrate by Merrow, van Dolah and Cristol [41] already cited, neither the presence of the nitrate ion nor of mercaptan was detected. For this reason the following reaction mechanism was proposed for the hydrolysis of nitric acid alcohol esters by means of hydrosulphide:

$$RONO_2 + S_x^{2\ominus} \longrightarrow RO^{\ominus} + NO_2S_x^{\ominus} \qquad (20)$$

$$NO_2S_x^{\ominus} + HS^{\ominus}(S^{2\ominus}) \longrightarrow NO_2^{\ominus} + HS_{x+1}^{\ominus} + (S_{x+1}^{2\ominus}) \qquad (21)$$

$$HS_{x+1}^{\ominus} + HS^{\ominus} \rightleftarrows HS_x^{\ominus} + HS_2^{\ominus} \qquad (22)$$

$$RO^{\ominus} + HS_x^{\ominus} \rightleftarrows ROH + S_x^{2\ominus} \qquad (23)$$

$$HO^{\ominus} + HS_x^{\ominus} \rightleftarrows H_2O + S_x^{2\ominus} \qquad (24)$$

or

$$RONO_2 + S_x^{2\ominus} \longrightarrow ROS_x^{\ominus} + NO_2^{\ominus} \qquad (25)$$

$$ROS_x^{\ominus} + HS^{\ominus} \longrightarrow RO^{\ominus} + HS_{x+1}^{\ominus} \qquad (26)$$

$$HS_{x+1}^{\ominus} + HS^{\ominus} \rightleftarrows HS_x^{\ominus} + HS_2^{\ominus} \qquad (27)$$

$$RO^{\ominus} + HS_x^{\ominus} \rightleftarrows ROH + S_x^{2\ominus} \qquad (28)$$

$$HO^{\ominus} + HS_x^{\ominus} \longrightarrow H_2O + S_x^{2\ominus} \qquad (29)$$

As shown by the eqns. (20–24) owing to the activity of the sulphide or polysulphide ion, the O—N linkage is broken to form alkoxide and thionitrate or polythionitrate ions. In the other reactions the influence exerted by sulphide on the oxygen atom, which results in the creation of nitrite ions, has been taken into account. Both schemes indicate that the nitrite ion is not produced by the reduction of the nitrate ion.

Recently the reactivity of nitric esters in the presence of hydrazine has been

investigated. These experiments are connected chiefly with the application of hydrazine as a liquid component in rocket fuels. In such fuels, nitric esters can play the part of the oxidizing and explosive component.

As long ago as 1896 Walther [43] observed that as the result of chemical reaction between ethyl nitrate and phenylhydrazine at an elevated temperature, aniline, ammonium nitrate and nitrogen are formed. If the reaction takes place in the presence of sodium ethoxide then, according to Bamberger and Billeter [44] even at room temperature nitrite ions, nitrogen, benzene, phenyl azide, azobenzene, nitrobenzene, aniline, acetic acid and acetaldehyde are formed.

Owing to the influence of hydrazine, at room temperature and in the presence of palladium or platinum as a catalyst, hexyl nitrate is transformed into the corresponding alcohol. Amongst other products nitrous oxide and nitrogen are formed during the same process (L. P. Kuhn [45]):

$$2C_6H_{13}ONO_2 + 2N_2H_4 \longrightarrow 2C_6H_{13}OH + N_2O + 3H_2O + 2N_2 \qquad (30)$$

If in this reaction hydrazine is replaced by methylhydrazine, then the hexyl nitrate forms not methyl hexyl ether but hexyl alcohol.

Merrow and van Dolah [46] investigated the behaviour of nitric esters in the presence of hydrazine and its derivatives. According to these authors nitric esters at room temperature and without catalysts react with phenylhydrazine very slowly even if the concentrations of the components are high.

Analysing the products of reaction between alkyl nitrates and hydrazine they detected nitrate and nitrite ions, a corresponding alcohol, alkyl hydrazine, nitrogen oxides, ammonia and traces of aldehyde. If the reaction is performed without solvents in an excess of hydrazine, reduction occurs. In an aqueous solution of alcohol the process of substitution predominates particularly when the concentrations of reagents are low.

Merrow and van Dolah also established that during the hydrolysis of β-chloroethyl nitrate, 1,3-dichloro-2-propyl nitrate, glycerol trinitrate or glycol dinitrate the gaseous products are evolved more vigorously than during the reaction of unsubstituted aliphatic nitrates.

Investigating the types of reaction between nitric acid esters and hydrazine Merrow and van Dolah endeavoured first of all to solve the problem of how nitric acid is formed since the answer could in effect make it possible to establish the position of the linkage to be broken off in an ester molecule. They have established experimentally that during the reaction between alkyl nitrates and hydrazine the nitrite ion is produced very quickly. Later it dwindles away as reaction proceeds. The creation of $NO_2^{\ominus}$ in this process can never arise from the removal of a hydrogen atom in the α-position, since only an insignificant amount of ester can follow the reaction (31) to form an aldehyde:

$$RCH_2ONO_2 \xrightarrow{N_2H_4} RCHO + H^{\oplus} + NO_2^{\ominus} \qquad (31)$$

Further, the nitrite ion cannot be the reduction product of the nitrate ion formed

in consequence of the rupture of the C—O bond since, for example, the NO_3-ion of sodium nitrate does not undergo any change in presence of hydrazine.

The $NO_2^{\ominus}$-ion might be formed from the nitrous acid ester if the latter was present as an impurity in the main reactant. Trials carried out with ethyl nitrite and n-butyl nitrite have demonstrated, however, that when these compounds are treated with an excess of hydrazine they do not undergo any chemical reaction accompanied by the formation of the nitrate ion.

According to Merrow and van Dolah the reaction between a nitric ester and hydrazine is performed in the way outlined below:

$$RONO_2 + H_2NNH_2 \longrightarrow RO^{\ominus} + H_2N{-}\overset{\oplus}{N}H_2{-}NO_2 \rightleftharpoons ROH + H_2N{-}NHNO_2 \quad (32)$$

$$H_2N{-}NH{-}NO_2 + H_2NNH_2 \longrightarrow H_2N{-}NH{-}NH{-}NH_2 + HNO_2 \quad (33)$$

$$H_2N{-}NH{-}NO_2 + H_2NNH_2 \longrightarrow HN{=}NH + N_2H_4 \cdot HNO_2 \quad (34)$$

$$H_2N{-}NH{-}NH{-}NH_2 \longrightarrow N_2 + 2NH_3 \quad (35)$$

$$NH{=}N{-}NH{-}NH_2 \longrightarrow HN_3 + NH_3 \quad (36)$$

$$2NH{=}NH \longrightarrow N_2 + H_2N{-}NH_2 \quad (37)$$

In the first stage of the reaction an alkoxyl anion and the nitrohydrazine cation are formed which afterwards react together to give the corresponding alcohol and nitrohydrazine. Nitrohydrazine reacts with excess hydrazine to produce tetrazene, nitrous acid and di-imid. Then the tetrazene decomposes to form ammonia and nitrogen; from di-imid on the other hand tetrazene, hydrazine and nitrogen are formed. Hydrazoic acid and ammonia are then formed as decomposition products of tetrazene.

Reactions (32–37) take place as a result of breakage of the N—O linkage, in a manner analogous to the breakage of the chemical bond between an acyl radical and an oxygen atom when esters of carboxylic acids are hydrolysed. Generally the linkage is broken off in this way when the n-alkyl esters of nitric acid are hydrolysed in an alkaline medium or when nitration is carried out with nitrates in the presence of bases, e.g. the nitration of aniline by means of ethyl nitrate in the presence of potassium ethoxide to yield phenylnitramine as its final product (Bamberger [47]).

The above reaction scheme between nitric esters and hydrazine or its derivatives is confirmed by the reaction of methylhydrazine and ethyl nitrate which yield methane (not ethane) and nitrogen. This indicates that the unstable monomethyl-di-imid should have been an intermediate product:

$$CH_3HNNH_2 + C_2H_5ONO_2 \longrightarrow CH_3N{=}NH + C_2H_5OH + HNO_2 \quad (38)$$

$$CH_3N{=}NH \longrightarrow CH_4 + N_2 \quad (39)$$

The gradual decreasing concentration of nitrous acid in the mixture of reagents can be explained as the result of the reduction process taking place under the influence of hydrazine:

$$HNO_2 + N_2H_4 \longrightarrow NH_3 + N_2O + H_2O \quad (40)$$

$$HNO_2 + N_2H_4 \longrightarrow HN_3 + 2H_2O \quad (41)$$

$$HNO_2 + HN_3 \longrightarrow N_2 + N_2O + H_2O \quad (42)$$

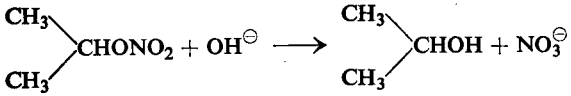
Benzyl nitrate reacts with hydrazine in the presence of solvents or without a solvent to give a range of substitution product: $C_6H_5CH_2HNNH_2$, $(C_6H_5CH_2)_2NNH_2$, $(C_6H_5CH_2)_2NNHCH_2C_6H_5$, $(C_6H_5CH_2)_2NN(CH_2C_6H_5)_2$.

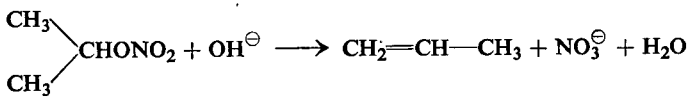
By application of benzylhydrazine, benzaldibenzylhydrazine

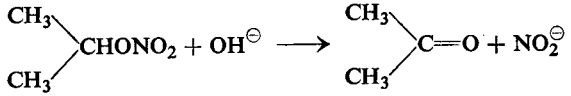
$$(C_6H_5CH_2)_2N—N=CHC_6H_5$$

has been obtained. It is not certain whether the compound formed was a product of reaction between benzaldehyde (formed by removal of a hydrogen atom in the α-position) and 1,1-dibenzylhydrazine, or an oxidation product of tribenzylhydrazine. Kenner and Wilson [48] have established that tribenzylhydrazine is very likely to be oxidized even by atmospheric oxygen.

In the presence of hydrazine the C—O linkages of tert-butyl nitrate undergo rupture almost exclusively to form isobutylene and hydrazine nitrate. During this reaction neither the presence of nitrogen nor of its oxides has been detected. By hydrolysing isopropyl nitrate in an alkaline medium, Baker has obtained 70–80% of isopropyl alcohol, 11–14% of propylene and 8–14% of acetone. If the reaction types (10, 11, 12) as suggested by Baker and Easty [40] are accepted, the hydrolysis process can be expressed by the following equations:


(43)


(44)


(45)

By hydrolysing isopropyl nitrate in a neutral medium only alcohol is formed.

Accepting the reaction (10) suggested by Baker and Easty in order to explain how the alcohol is formed, it must be assumed that the process consists of two successive stages. First a carbonium ion is formed:

$$RONO_2 \longrightarrow R^{\oplus} + ONO_2^{\ominus} \quad (46)$$

and then an addition-exchange process takes place:

$$R^{\oplus} + H_2O \longrightarrow ROH + H^{\oplus} \quad (47)$$

No analogous reactions take place with carboxylic acid esters. Cristol and his co-workers [49] therefore suggest that initially an alkoxyl ion is formed and afterwards the corresponding alcohol and nitrate ion are produced:

$$RO—NO_2 + OH^{\ominus} \longrightarrow RO^{\ominus} + HONO_2 \longrightarrow ROH + NO_3^{\ominus} \quad (48)$$

Cristol and his co-workers have carried out the hydrolysis of the optically active 2-octyl nitrate in alkaline and neutral media. The alkaline hydrolysis was performed in the presence of sodium hydroxide both in 92.6% ethanol, where the participation of the ethoxide ion should be taken into account, and in a 64% aqueous solution of dioxane. The neutral hydrolysis was carried out in a 70% acetone solution in the presence of calcium carbonate.

By esterifying (+)2-octanol using a mixture of nitric and sulphuric acid, it was established that the nitrate produced did not undergo inversion. The (+)2-octyl nitrate obtained was heated during a period of 50 hr in a 10% alcoholic solution of sodium hydroxide. The optical rotation of all the reaction products was nil. Analysis by means of Grignard's reagent indicated 45.6% of 2-octanol, 39.8% of ketone and 14.6% of ether (by difference). A sample of the alcohol contained 76% of (+)2-octanol and 24% of racemate, i.e. 88% of (+)2-octanol and 12% of (−)2-octanol.

On the basis of these results and taking into account the effect of the ethoxide ion, the authors propose the following reaction schemes:

$$EtO^{\ominus} + R{-}ONO_2 \longrightarrow EtOR + NO_3^{\ominus} \tag{49}$$

$$EtO^{\ominus} + RO{-}NO_2 \longrightarrow EtONO_2 + RO^{\ominus} \tag{50}$$

During the hydrolysis of 2-octyl nitrate according to eqn. (49), ethyl 2-octyl ether is formed which should have a rotation contrary to that of the unreacted nitrate. On the other hand from the reaction (50) which resembles to some extent eqn. (48), an alcohol of the same rotation and a product of transesterification is obtained. Cristol does not explain in detail the mechanism of the reaction of transesterification (ester group exchange reaction). None the less an assumption can be made that it may occur only in the presence of nitronium cation $NO_2^{\oplus}$. Further, the reaction leading to the formation of ketones has not yet been explained. Most probably it is analogous to the scheme (12) in which a hydrogen atom attached to the α-carbon atom is split off after a O—N linkage is broken:

$$\begin{array}{l} R{-}CH{-}CH_3 \\ \quad\quad | \\ \quad ONO_2 \end{array} + OH^{\ominus} \longrightarrow \begin{array}{l} R{-}C{-}CH_3 \\ \quad\quad \| \\ \quad\quad O \end{array} + NO_2^{\ominus} + H_2O \tag{51}$$

The experiment of hydrolysing 2-octyl nitrate in a dioxane solution has been carried out with a laevo-rotatory ester. In the reaction products 2-octanol forms as the main product with some 2-octanone and a little unchanged 2-octyl nitrate. The rotation of the reaction product amounted to −3.77°, and the alcohol consisted of a mixture containing 42% of (−)2-octanol and 58% of racemate, i.e. 71% (−)2-octanol and 29% (+)2-octanol.

By hydrolysis of a dextro-rotatory 2-octyl nitrate in a neutral medium, this compound has been decomposed to yield a laevo-rotatory product containing 13% of 2-octanone and 87% of 2-octanol, the latter comprising 71% of (−)2-octanol and 29% racemate, i.e. 85.5 parts of laevo-rotatory and 14.5 parts of dextro-rotatory alcohol.

It can be concluded from these experimental results that in alkaline media the 2-octyl nitrate behaves like a typical ester (Day and Ingold [50]). In neutral media, on the other hand, it behaves like an alkyl halogenide or like an ester of sulphuric acid.

Cristol also established in the work cited that the hydrolysis of 2-octyl nitrate cannot be performed with dilute sulphuric acid. In the presence of 10% sulphuric acid as much as 99 parts of alcohol having the same rotation as the original nitrate were formed. With 70–90% sulphuric acid, 2-octanone and nitrogen oxides were formed.

According to Merrow and van Dolah [51] (+)2-octyl nitrate reacts with hydrazine at room temperature to yield 84% (+)2-octanol, whilst by the reaction of the laevo-rotatory nitrate and ammonium polysulphide as much as 99 parts of (−)2-octanol are produced. The fact that to a large extent the original rotation was preserved indicates that in the cases cited the initial step was rupture of the N—O bond.

Further experiments on the hydrolysis of *cis*- and *trans*-cyclohexanediol dinitrates have been carried out by Merrow and van Dolah. The *trans*-1,2-cyclohexanediol dinitrate in the presence of hydrazine is transformed exclusively into *trans*-1,2-cyclohexanediol. Similarly the *cis*-isomer does not change its configuration if treated with ammonium sulphide. All these observations confirm the conclusion mentioned above.

Baker [52], who investigated the influence of nucleophilic reagents on benzyl nitrate in anhydrous alcohol, has established that two parallel reactions proceed simultaneously (Y is a hydrolysing agent):

$$Y^{\ominus} + C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CH_2Y + NO_3^{\ominus} \tag{52}$$

$$Y^{\ominus} + C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CHO + NO_2^{\ominus} + HY \tag{53}$$

The latter reaction takes place via an intermediate stage:

$$C_6H_5CH_2ONO_2 \longrightarrow C_6H_5CH_2O^{\oplus} + NO_2^{\ominus} \tag{54}$$

If the reaction medium contains an aroxide as well as the alkoxide ions, then it is mainly the second of these two ions, which is more nucleophilic, that takes part in the chemical reaction. The way in which both ions are formed from the solvent has been described by Baker according to eqn. (55):

$$Y^{\ominus} + EtOH \longrightarrow HY + EtO^{\ominus} \tag{55}$$

Baker controlled the kinetics of the reactions (52) and (53) in the presence of ethyl alcohol, phenol and its mononitro derivative.

On the basis of experiments on the hydrolysis of numerous esters of inorganic acids carried out by Anbar *et al.* [53] this reaction has been defined by means of the three following equations:

$$Y^{\ominus} + —C—O—X \longrightarrow —CY + OX^{\ominus} \tag{56}$$

$$Y^{\ominus} + —C—O—X \longrightarrow —CO^{\ominus} + XY \tag{57}$$

$$Y^{\ominus} + H—C—O—X \longrightarrow C{=}O + HY + X^{\ominus} \tag{58}$$

According to eqn. (56) a nucleophilic substitution takes place, i.e. the component Y is attached to the α-carbon atom. Similarly in reaction (57) $Y^{\ominus}$ attaches itself to the central atom of the X-group (such as the nitrogen atom in the nitro group). The last equation illustrates a typical oxidation process, producing an aldehyde or ketone with the removal of a hydrogen atom attached to the α-carbon atom.

Equations (56) and (57) are analogous to (10) and (12) proposed by Baker; and (58) resembles (50).

In order to generalize on the conditions that determine the direction of the hydrolysis process and to deduce adequate conclusions, several examples of the hydrolysis of esters of inorganic acids are quoted below together with the probable reaction type. Hydrolysis was performed in an alkaline medium using water labelled with the ^{18}O-isotope.

tert-Butyl hypochlorite	(57)
Triphenylmethyl chlorate, bromate, iodate	(58)
Triphenylmethyl perchlorate	(56)
n-Butyl nitrate	(57)
tert-Butyl nitrate	(57)
Triphenylmethyl nitrate	(57)
n-Butyl nitrate	various reactions
n-Octyl nitrate	various reactions
tert-Butyl nitrate	(56)
Triphenylmethyl nitrate	(56)

It is clear from this comparison that triphenylmethanol esters of weaker acids undergo the reaction of hydrolysis as shown in the scheme (57). Depending on the kind of radical, during the hydrolysis of strong acid esters either the R—O bond is broken (scheme 56) or a mixture of reaction products is formed as indicated by the schemes mentioned. The reaction goes more readily with esters of weak acids, as the radical's influence is not prominant. With strong acid esters and the more electronegative (iso-) radicals hydrolysis proceeds in accordance with eqn. (56). Esters of strong acids and those which contain less electronegative radicals do not demonstrate any definite direction of hydrolysis.

The above conclusions find further confirmation in the results of hydrolysis of sugar nitrates that have been carried out by Ansell and Honeymann [54], and in experiments to nitrate cyclic ketones by means of optically active nitrates made by Horn and Shirner [55].

Comparing triphenylmethanol esters of hydroxy-acids we can establish that the higher oxidation compounds (being at the same time also stronger acids) are hydrolysed according to the reaction scheme (56), whilst with compounds having a lower degree of oxidation the process follows eqn. (57). For instance, among the following esters: RO—Cl, RO—ClO, RO—ClO_2, RO—ClO_3, the change of reaction type occurs between chloric and perchloric acid esters. Likewise nitric esters react mainly according to the scheme (57). This question has been investigated particularly by Allen [56]. The direction followed by the hydrolysis process depends upon many factors, including the type of radical and the reaction medium.

The above results are supported by Brönsted's theory since with esters of strong acids—owing to their tendency to donate protons—favourable conditions are created for splitting the R—O bond and producing the carbonium ion.

If the reaction formulated in eqn. (56) takes place and if $Y^{\ominus}=RO^{\ominus}$ then primarily ether is formed. If on the other hand $Y^{\ominus}=\diagup C^{\ominus}$ or $\diagup N^{\ominus}$ an alkylation process takes place. If the reaction type conforms with the scheme (57) and if $Y=RO^{\ominus}$ then a reaction of transesterification takes place, whilst the presence of $Y^{\ominus}=\diagup C^{\ominus}$ or $Y^{\ominus}=\diagup N^{\ominus}$ stimulates the nitration process. So, for instance, n-butyl nitrate treated with benzyl cyanide in an alkaline medium produces sodium nitrophenylmethanecarbonitrile in about 70% yield. This provides evidence that the predominating reaction should be defined by the eqn. (57) as shown by the following example:

$$C_6H_5CH_2CN + C_4H_9O{-}NO_2 \xrightarrow{NaOH} \underset{\displaystyle NO_2Na}{\underset{\|}{C_6H_5CCN}} + C_4H_9OH + H_2O \qquad (59)$$

In the presence of sodium ethoxide tertiary butyl nitrate reacts with benzyl cyanide to form exclusively butyl ethyl ether and sodium nitrate. In this case no transesterification occurs. Thus the reaction proceeds in accordance with eqn. (56).

With reaction (56) a competing process to form olefins occurs, in which the chemical bond R—O is broken, as outlined in scheme (11). The formation of olefins, as mentioned above, depends primarily on the character of the alkyl group and also on the conditions of reaction.

Tertiary alkyl esters react mainly according to (56) and (57). During hydrolysis performed in accordance with the latter reaction in the presence of $Y^{\ominus}=RO^{\ominus}$ a process of transesterification takes place as shown by the equation below:

$$RO^{\ominus} + \underset{|}{\overset{|}{-C-}}O-X \longrightarrow ROX + \underset{|}{\overset{|}{-C}}O^{\ominus} \qquad (60)$$

Thus in a mixture of a tertiary ester with a secondary or primary alcohol, esters of these alcohols can be produced. Immediately they have been formed, the esters can undergo further chemical combination, as indicated in eqns. (57) and (58). The original ester can be transformed in the manner indicated by eqn. (58) if it possesses a hydrogen atom attached to the α-carbon atom. In any other case alcohol formed as the reaction proceeds cannot be oxidized.

According to reports of Kharasch *et al.* [57] the chemical reaction defined by the scheme (58) occurs when conditions favour the formation of radicals in the solution of an ionizable solvent and when the $X^{\ominus}$-anion thus formed is sufficiently stable.

According to Kharasch, primary and secondary nitrates which have been hydrolysed in accordance with the scheme (57) produce a certain quantity of oxidation

product. On the other hand tertiary butyl nitrite can undergo the reaction of transesterification. However, it does not react as suggested by the eqn. (58), since the $NO^{\ominus}$ ion is not sufficiently stable.

REDUCTION OF NITRIC ESTERS

There are various different methods for reducing nitric esters and thereby removing their nitro group. In most cases the original alcohols are recovered as result of the reaction.

The oldest and most popular method is reductive hydrolysis by means of alkaline sulphides or hydrosulphides, for instance sodium or ammonium sulphide or the corresponding hydrosulphide, as discussed above in connection with the question of hydrolysis (pp. 9–10). According to Oehman *et al.* [103] acid hydrolysis of nitroglycerine follows a course similar to that of eqn. (58). Hydrolysis with sulphuric acid (even in the presence of nitric acid) may lead to a transesterification and formation of sulphuric acid esters [104].

As for other methods the following reduction processes are known: in acetic acid by means of iron (Oldham [58]), in acetic acid with iron and zinc (Dewar and Fort [59]), catalytic hydrogenation under pressure over a palladium contact (L. P. Kuhn [60]), or by means of hydrazine in the presence of palladium or platinum. Applying the last method a good yield of alcohol accompanied by NO, N_2 and H_2O has been obtained by L. P. Kuhn [45]. The reduction can be carried out by means of zinc in the presence of acetic anhydride (Hoffman, Bower, Wolfrom [61]).

Electrolytic reduction of nitric esters has also been reported (Kaufman, H. J. Cook and S. M. Davis [62]).

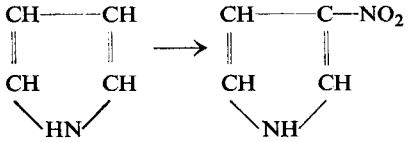
A new manner of reducing nitric esters which consists in the application of lithium aluminium hydride has been described by Soffer, Parrotta and di Domenico [63]. The reaction is performed in an ether solution from which alcohol is recovered quantitatively. Among the reaction products in addition to alcohol the presence of NO_2 group and ammonia have been established by these authors. To complete the reaction, 3.3 molecules $LiAlH_4$ are necessary for each ONO_2 group. Simultaneously the same method has been applied by Ansell and Honeyman [54] to reduce the sugar acetal nitrates in a boiling ether solution. This reaction proceeds very slowly. It sometimes takes 50 hr. However, pure acetal alcohol is formed in good yield.

SOME OTHER REACTIONS OF NITRIC ESTERS

In the presence of sodium or potassium ethoxide, nitric esters react with substances containing an active methylene group to form salts of aci-nitro compounds (Wislicenus [64]) as quoted above in eqn. (59). Esters are hydrolysed on this occasion.

Evidently, from these salts pure nitro compounds can be obtained. This property of nitric esters makes it possible to use them as nitrating agents (Vol. I). For

instance pyrrole and indole can be nitrated by means of ethyl nitrate. In effect a β-nitro compound is produced:



Like nitrous esters, alkyl esters of nitric acid enter into reaction with a surplus of Grignard's reagent to form N-dialkylhydroxylamine.

Certain nitric esters are capable of forming addition products with aromatic nitro compounds (see pp. 167, 169), as indicated by T. Urbański [65].

An interesting property of nitric esters, namely their ability to catalyse certain reactions of addition polymerization has been reported recently. Initially this observation was made by Rogovin and Tsaplina [66] while polymerizing styrene and methyl methacrylate in the presence of nitroglycerine. The latter amounted to 5–20 parts by weight corresponding to about 10% of the polymerized substance. As a result of the increased polymerization speed, the molecular weight of the polymer is smaller than if polymerization is carried out slowly.

Hicks [67] confirmed these observations for the methyl methacrylate–glycol dinitrate system. The substances have been used at mole ratios ranging from 0.07 to 5.9. Working at temperatures of 25, 60, 80 and 90°C it was established that from 60 to 90°C partial decomposition of nitroglycol takes place and free radicals initiating polymerization are formed.

An interesting exception reported by Rogovin and Tsaplina concerns vinyl acetate which when exposed to the influence of nitric esters, polymerizes very slowly. The ester radicals $\cdot NO_2$, $\cdot ONO_2$ and ions $NO_2^{\oplus}$, $ONO_2^{\ominus}$, do not seem to influence appreciably the rate of polymerization and the catalytic action of nitric esters is not produced by the presence of $O-NO_2$ groups.

However, the views of Rogovin and Tsaplina should be revised in the light of recent experiments of Szyc-Lewańska and Syczewski [67a]. They found that glycols and glycerol exhibit the same catalytic action as their nitric esters on the polymerization of styrene and methyl methacrylate. This seems to suggest that the molecules

$$\begin{matrix} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{matrix} \quad \text{and} \quad \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$$

behave in an identical way through the formation of the free radicals

$$\begin{matrix} CH_2O\cdot \\ | \\ CH_2O\cdot \end{matrix} \quad \text{and} \quad \begin{matrix} CH_2\cdot \\ | \\ CH_2\cdot \end{matrix}$$

or through alkoxy $(CH_2O)_2^{2\ominus}$ and alkylene $(CH_2)_2^{2\oplus}$ ions.

FORMATION OF NITRIC ESTERS

The simplest and most commonly used method of preparing nitric esters consists in the "O-nitration" reaction of alcohols with nitric acid, usually in the presence of sulphuric acid. The reaction is accompanied by reversible hydrolysis, which is typical of esterification reactions. It is very likely that the main nitrating agent is the nitronium ion $NO_2^{\oplus}$ (nitryl cation). It acts through electrophilic substitution. The presence of sulphuric and perchloric acids in the esterifying mixed acid favours the esterification, as it increases the concentration of $NO_2^{\oplus}$ ion.

When investigating the O-nitration of glycerol Ingold *et al.* [68] established that primary alcoholic groups are attacked with $NO_2^{\oplus}$ very quickly and the reaction is of zero order. The secondary alcoholic group reacts at a lower rate and the reaction is of the first order.

It was observed that the presence of sulphuric acid promotes the hydrolysis of esters (e.g. [104, 107, 109]). The rate of hydrolysis is for the most part significantly lower than the esterification rate. Moreover, as already discussed above, in addition to the main reaction producing alcohol and nitrating acid, the hydrolysis process is generally accompanied by side reactions. Acids other than sulphuric, or perchloric [104], e.g. acetic [106] or phosphoric, if present in the esterifying mixture, hydrolyse esters to a markedly smaller extent than sulphuric acid. The acid make up of an esterification mixture in industry is established experimentally. Economic factors also plays a part here.

In addition to these chemical reactions outlined above oxidation reactions also take place during the esterification process.

According to certain authors the oxidation reaction is facilitated by the presence of nitrogen dioxide. Since the oxidation reaction is undesirable, attention should be paid to the concentration of nitrogen dioxide in the nitrating acid in order to maintain it as low as possible. Pure nitrogen dioxide is a very strong oxidizing agent.

Kaverzneva, Ivanov and Salov [69] found that isopropyl alcohol, under the influence of dinitrogen tetroxide at normal temperature, is transformed into acetone. Ethylene glycol is oxidized rapidly by it to oxalic and glycolic acids.

Owing to oxidation by nitrogen dioxide, 1,2-propanediol is transformed into hydroxyacetone and pyruvic acid. The authors report that no lactic acid is produced, which is evidence that in the first place the secondary alcohol groups are oxidized.

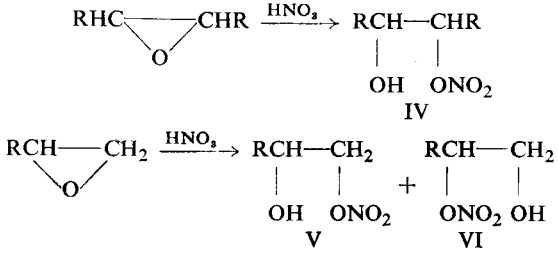
Likewise the primary hydroxy groups of cellulose are oxidized to form the --COOH groups, while the secondary ones give CO-groups (see p. 347).

O-Nitration is an exothermic reaction. Approximate calculations which have been made (Kagawa [70]; Calvet and Dhers-Pession [71]) on the basis of esterifying methyl alcohol and cellulose indicate that the esterification of one hydroxyl group is accompanied by the development of 2 ± 0.2 kcal of heat (see pp. 46, 147).

Nitric esters are produced by the reaction between nitric acid and derivatives of ethylene oxide (Hanriot [72]; L. Smith, Wode, Widhe [73]). According to

Nichols, Magnusson and Ingham [74] oxides having the structure RHC(O)CHR and RHC(O)CH_2 can be nitrated by means of 30% nitric acid in presence of ammonium nitrate, the latter being a component counteracting side reactions of oxidation.

If 1.5 mole of nitric acid for 1 mole of oxide are used then according to the kind of oxide used monoesters (IV), (V) and (VI) will be obtained with 40–60% theoretical yield:



When acting with dinitrogen tetroxide on ethylene oxide and homologues followed by hydrolysis a nitric ester of the type (IV) is formed (Pujo *et al.* [108], Rossmy [75]).

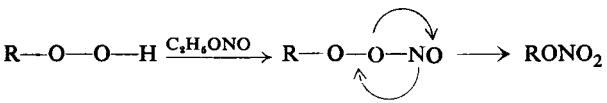
In some cases, in the laboratory a method of indirect introduction of ONO_2 group through the action of silver nitrate upon alkyl halides can be used.

$$RCl + AgNO_3 \longrightarrow RONO_2 \qquad (61)$$

Alkyl nitric esters can also be formed by acting on alkylhydroperoxide with ethyl nitrite:

$$R{-}O{-}O{-}H + C_2H_5ONO \longrightarrow RONO_2 + C_2H_5OH \qquad (62)$$

The reaction was discovered by Baeyer and Villiger [75a] and studied in a more detailed way by Criegee and Schnorrenberg [1a]. They suggested that the mechanism of the reaction is:



NITRIC ESTERS AS EXPLOSIVES

Alkyl esters of nitric acid are very strong explosives. Their oxygen balance is obviously higher than in the case of explosive nitro compounds containing the same number of carbon atoms and nitro groups. Moreover, in many esters the ratio of O-nitro groups to carbon atoms can be more favourable than in aromatic nitro compounds. Many nitric esters possess as many nitro-ester groups as carbon atoms. This is why such esters of nitric acid as e.g. nitroglycerine, nitroglycol and pentaerythritol tetranitrate are among the most powerful explosives, their explosive strength exceeding that of such widely used nitro compounds as TNT. The disadvantage of nitric esters is that they are more sensitive to shock and friction and to high temperature than nitro compounds. Furthermore they can undergo hydrolytic decomposition.

CHEMICAL STABILITY

The stability of an explosive may be regarded as its capacity to remain unchanged during a longer period of storage. The problem of stability is of primary importance with nitric esters, since their structure exposes them to the risk of being hydrolysed. However, the purer the ester, the smaller the danger of hydrolysis. It is of exceptional importance to keep the ester free from acids and strong bases which could cause decomposition. Certain nitric acid alkyl esters exist that are insufficiently stable even in the purest form. Their low stability results, of course, from their chemical structure, as for instance, with methylene glycol dinitrate. For the most part nitric esters of the nitroglycerine, pentaerythritol tetranitrate and nitrocellulose type are characterized by an adequate stability provided they are in a pure form.

Ropuszyński [76] suggests two distinct aspects of stability, namely *chemical* stability—which ought to be understood as the stability of the pure chemical compound; and *practical* stability—that characterizes a product "stabilized" by methods applied in practice.

In accordance with these definitions a substance possessing good chemical stability may still be of insufficient practical stability if it is not fairly pure.

Hydrolytic decomposition has already been discussed. A different type of decomposition of nitric esters occurs at elevated temperatures. More detailed information concerning this type of decomposition will be included in the descriptions of the individual esters properties, in particular those of nitroglycerine and nitrocellulose.

The decomposition of esters at elevated temperatures is of exceptional practical importance, since it has often been responsible for accidents. Investigations of the decomposition of esters at elevated temperatures by laboratory tests serve as a rapid method of estimating their stability.

A number of authors have tried to express the decomposition rate of nitric esters in mathematical formulae. Thus Berthelot [77] expressed the relation between the decomposition rate of nitric esters and the temperature as:

$$V = Kt + C \tag{63}$$

where: V—the rate of reaction in mg of nitrogen produced from 1 g of the substance; t—temperature; K, C—constants, of which C depends on the purity of the substance and its degree of nitration; K depends on the nature of the substance.

Later the relation between the decomposition of alkyl esters of nitric acid and the temperature was formulated (Will [78]) by means of the eqn. (64):

$$\log N = a + b \cdot 0.9932^t \tag{64}$$

where: N—the quantity of mg nitrogen evolved from a 2.5 g sample of the substance in 15 min; a, b—constants; t—temperature.

According to Will for guncotton the following constants have been found: $a = 8.8842$, $b = 22.86$.

It is necessary to take into consideration the fact that the decomposition of nitric esters has an autocatalytic character: water and nitrogen dioxide formed during the decomposition lead to the formation of nitric and nitrous acids which accelerate the reaction of decomposition of the nitric ester. The influence of nitric acid on the rate of decomposition of nitroglycerine was studied by Roginskii [79] and is described below.

METHODS OF DETERMINING THE STABILITY OF NITRIC ESTERS

All methods of determining the stability of explosives and particularly of nitric esters consist in examining the behaviour of the substances at an elevated temperature. It is obvious that the most reliable methods of determining stability are those which are carried out at lower temperatures approaching the ordinary room temperature.

It is known and has been demonstrated by several authors (by Sapozhnikov *et al.* [80] for nitrocellulose; by Lukin [81] for nitroglycerine) that change of temperature alters the composition of the reaction products. As the result of numerous experiments, particular temperatures were chosen for definite nitric esters. Thus, owing to the greater ease of decomposition of nitroglycerine as compared with nitrocellulose the high temperature heat test for nitroglycerine is carried out at a temperature lower than that for nitrocellulose (120 and 132° C respectively).

The disadvantage of carrying out a stability test at low temperature is of course the very low rate of the reaction, and hence the very long time required to complete the experiment. Low temperature tests are applied in special cases only, and methods employing elevated temperatures are in general use.

Two main categories are distinguished: (a) qualitative, and (b) quantitative ones.

A full description of the methods of determining the stability of explosives are given in books dealing with analysis of explosives, such as: Kast and Metz [82], Clift and Fedoroff [83], Olsen and Greene [84], and Avanesov [85].

Qualitative tests

The qualitative tests usually consist in determining the heating period necessary to produce a noticeable decomposition of the compound or decomposition of the impurities present in the sample. The higher the stability, the longer the determined time.

Heat test (Abel test). The oldest and the most popular qualitative test is the heat test introduced in Great Britain by Abel in 1865 [86]. It is called the "Abel test" on the Continent of Europe and the "KI starch test" in the U.S.A. It consists in warming a sample of nitroglycerine or nitrocellulose (or dynamite or smokeless powder) in a test tube in which a potassium iodide–starch paper moistened with aqueous glycerol solution is suspended (Fig. 1). Warming is carried out until the

test paper acquires a faint brown colour. A thermostatic bath is used for this purpose.

The original British heat test [87] consists in heating the samples: 2 cm^3 of nitroglycerine at 160°F (71.1°C) or 1.3 g of nitrocellulose at 170°F (76.7°C), or 1.6 g of cordite at 180°F (82.2°C). The time the explosive should stand the test is 15 min, 10 min and 30 min respectively.

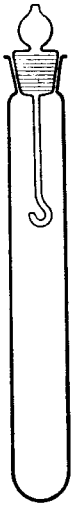


FIG. 1. Test tube for the Abel heat test, Soviet pattern [85].

In various countries different standards are accepted; e.g. in the U.S.S.R. a temperature of 75±0.5°C and in U.S.A. 65.5±1°C is applied. In Germany more sensitive zinc iodide–starch test paper is used (p. 77).

It is obvious that the heat test does not necessarily indicate the beginning of the decomposition of the substance. More often it indicates the presence of unstable impurities (e.g. residual nitrating acid) or unstable by-products more readily decomposed than the substance itself.

The high sensitivity of the test and its simplicity are of great importance and these facts account for the popularity of the method as a test of determining the purity of nitroglycerine and nitrocellulose. The sensitivity of the test is considerably reduced when mercuric salts (e.g. $HgCl_2$) are present in nitrocellulose. This is the result of the reaction of mercuric salts with iodine.

Litmus test (Vieille test). This test introduced by Vieille [88] consists in warming a sample of nitrocellulose (2.5 g) or smokeless powder in a hermetically sealed test tube (Fig. 2) in presence of a band of blue litmus paper inserted within the tube. The tube is kept in a thermostat warmed to 110°C. The temperature inside the test tube is 108.5°C. In U.S.S.R. the temperature of the thermostat is 106.5°C. The blue paper should not turn definitely red in less than 7 hr.

When smokeless powder is tested the sample is warmed to 108.5°C for several

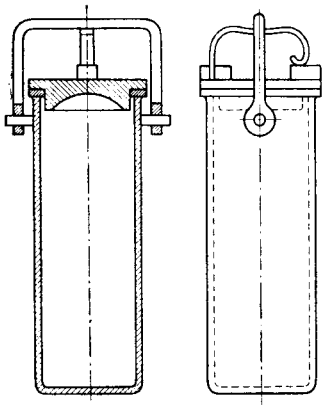


FIG. 2. Tube for litmus test (Vieille test).

days in succession but no longer than 10 hr a day (this is described in detail in Vol. III).

Heat test at 134.5°C. This heat test is in use in the U.S.A. A sample of 2.5 g of nitrocellulose or nitrocellulose powder ("single base powder") is kept in a long test tube in a constant temperature bath regulated to 134.5 ± 0.5°C. A band of methyl violet (rosaniline acetate with crystal violet) test paper is kept over the surface of the sample. The test paper should not change to "salmon" colour before 30 min and no visible NO_2 vapours should be detected before 45 min.

The test is usually continued for a total period of 5 hr, during which no explosion should occur.

Nitroglycerine powder ("double base powder") is tested at 120°C, the duration of the test being the same.

Silvered Vessel test. The so-called "Silvered Vessel test" is a stability test that consists in determining the period of heating necessary to cause exothermic decomposition of the substance. It is usually limited to determining the stability of smokeless powder and is described in Vol. III.

It was suggested by J. B. Taylor [89] as a method for the determination of the stability of nitrocellulose at 135°C. Nitrocellulose can be accepted as stable when, after 45–60 min heating, the temperature of the sample is not higher than the temperature of the thermostat by 1.1°C.

Qualitative tests at lower temperature ("Warmlagermethode") are carried out with powders only and are described in Vol. III.

Quantitative tests

Loss of weight. One of the oldest and simplest quantitative methods is the determination of the loss of weight of a sample heated at a constant temperature. The original Sy-test [90] used in the U.S.A. for determining the stability of nitrocellulose and nitrocellulose powder ("U.S. Ordnance Department 115° Test") consisted in heating a sample of the substance on a watch-glass at 115 ± 0.5°C.

Heating is carried out for 8 hr a day. During the first day the sample should loose only volatile substances (moisture and residual solvent). After that the loss of weight should not be greater than 1% a day during the next six days. A loss of 1% or more should be reached on the eighth day. The total loss of weight should be less than 10%.

In the U.S.S.R. the method was modified by using lower temperatures: $75\pm\pm0.5$°C or 95 ± 0.5°C. A sample of 15 g is kept in a 50 ml flask fitted with a cork provided with tubular orifice (Fig. 3). The flask with the sample is weighed every

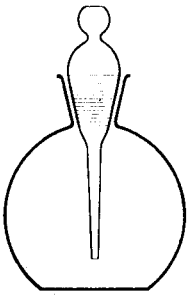


FIG. 3. Flask for determination of loss of weight (Avanesov [85]).

24 hr and the results are plotted on a diagram. After a certain time an increase in the loss of weight indicates that decomposition has become more rapid. That time is taken as a criterion of the stability of the substance.

In order to eliminate the necessity of removing the sample from the constant temperature chamber for weighing Guichard [91] introduced the use of an automatic balance which allows the weight of the sample to be recorded continuously.

Will test. Will [78] developed a method which consists in determining the volume of nitrogen evolved from nitrocellulose when kept at 135°C, gaseous products being removed by a stream of CO_2. The nitrogen oxides evolved during decomposition are reduced by hot copper and CO_2 is absorbed by a concentrated solution of potassium hydroxide. The volume of N_2 is recorded every 15 min. The test lasts 4 hr. The method was very useful for research but was difficult to apply as an everyday control of stability. Besides, the fact that nitrogen oxides are removed from the sample by the stream of CO_2 creates conditions which differ from those existing during storage of nitrocellulose or smokeless powder, when all the decomposition products remain in contact with the parent substance.

Bergmann and Junk test. The Bergmann and Junk [92] test consists in determining the quantity of $NO+NO_2$ lost by the sample (2 g of nitrocellulose or 5 g of nitrocellulose powder) when heated at 132°C for 2 hr. The test tube is closed at one end with a hydraulic seal (Fig. 4). The latter may be ball shaped (*a*) or (more frequently) bell shaped (*b*). After the test, the tube is withdrawn from the thermostat and cooled to the room temperature. Water is sucked into the tube, which is then

filled up with more water to the 50 ml mark. The solution is either titrated or its NO content determined by the Schulze–Tiemann method, after the solution has been oxidized with potassium permanganate.

One gramme of well stabilized high nitrated nitrocellulose or collodion cotton should not give off more than 2.5 or 2.0 cm^3 of NO, respectively.

The Bergmann and Junk tubes can be used to determine the pH of the solution obtained after heating nitric esters for varying times, e.g. 1, 2, 4 and 6 hr. This

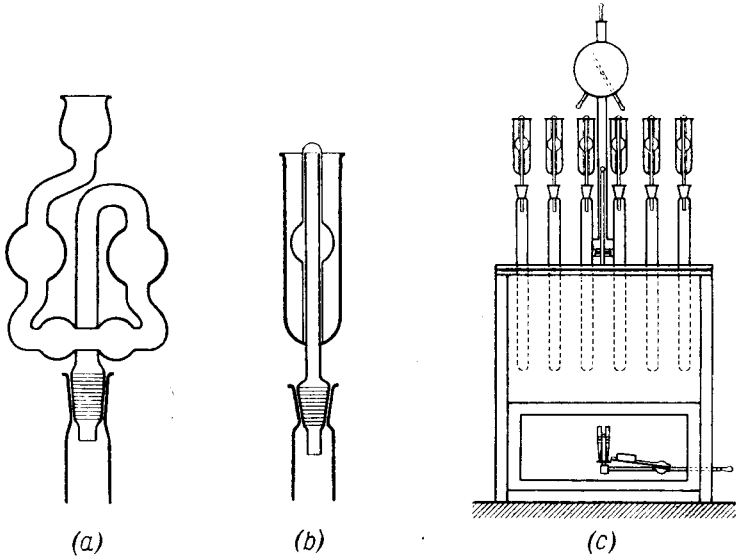


FIG. 4. Tubes for Bergmann and Junk test: (a) with balls, and (b) with tubular ending, (c) thermostat with tubes.

makes it possible to draw a curve showing the progress of decomposition of the substance. This method of determining the stability of the esters and smokeless powders was suggested by Hansen [93] and is frequently used for more detailed examination of the stability of nitric esters or powders.

Most nitric esters are subjected to heating at 120–132°C. In the case of nitroglycerine and nitroglycerine-like explosives, and also of nitrostarch, a temperature of 110–120°C is used.

Instead of a pH determination, the conductivity of the aqueous solution of the decomposition products can also be measured (e.g. Phillip [94]; de Bruin and Pauw [95]; Grottanelli [95a]). This, however, is less suitable for routine work.

Manometric test. The idea of measuring the pressure of the gaseous products evolved during decomposition of explosives on storage or heating was known as early as in the middle of the last century. It was mentioned by Abel [96] in his classic work on the stabilization of nitrocellulose. Ph. Hess [97] examined the decomposition of nitrocellulose at 70°C and measured the pressure of the decomposition products by means of a mercury manometer. Mittasch [98] applied the same idea

when studying the kinetics of decomposition of nitrocellulose. The first apparatus for routine stability measurement based on this principle was introduced by Obermüller [99] and further improved by Obermüller and Pleus [100].

The main disadvantage of the method consisted in the condensation of some of the products of decomposition in the tubes connecting the container with the manometer. This was overcome by Taliani [101] in his manometric method. The

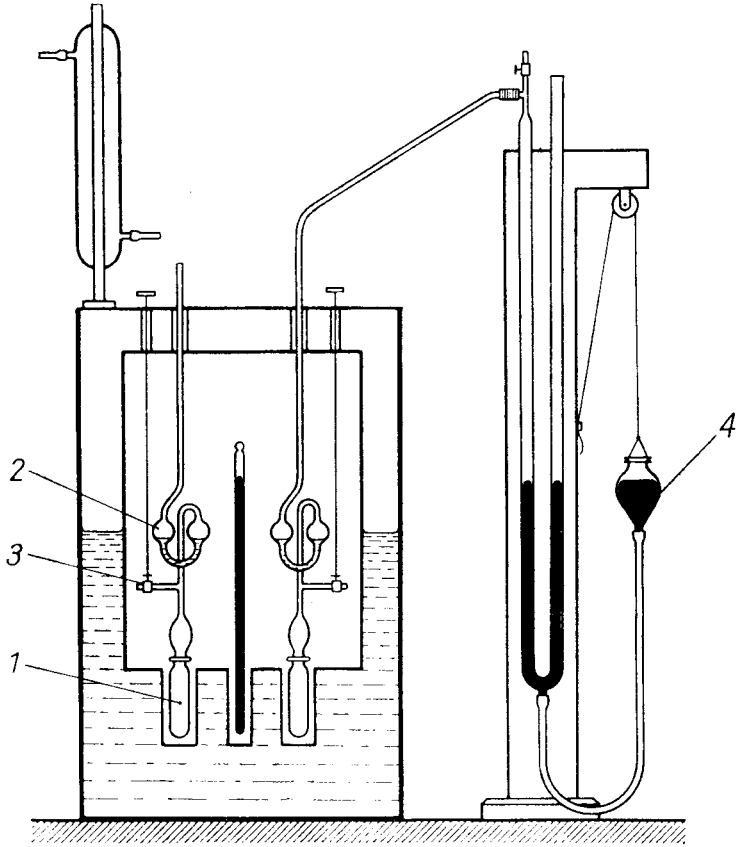


FIG. 5. Taliani test apparatus: *1*—tube with a test sample, *2*—hydraulic closure, *3*—stopcock.

main feature of this method (Fig. 5) consists in warming the sample of 1.3 g (*1*) to 135°C at a constant volume which is maintained by the U-tube (*2*) filled with liquid paraffin. The stopcock (*3*) is closed after the temperature has become uniform and then the pressure is increased by raising the bulb (*4*) to maintain the same level of paraffin oil in both branches of the U-tube (*2*). The experiment is stopped after 300 mm Hg pressure is reached. Goujon [102] modified the method, adopting a pressure of 100 mm Hg as the end of experiment.

The method of Taliani–Goujon is very useful, although by working under relatively elevated pressure it creates specific conditions which differ from those existing during the storage of explosives.

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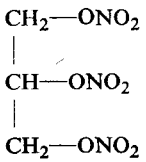
CHAPTER II

GLYCEROL TRINITRATE (NITROGLYCERINE)

ESTERS of monovalent alcohols and nitric acid do not play a large part as explosives. Among the polyvalent alcohol esters most useful for that purpose glycerol nitrates and glycol nitrates are especially important.

NITROGLYCERINE



Nitroglycerine (NG), strictly glycerol trinitrate is one of the most widely used explosives. It is the main component of high explosives such as dynamites, as well as an ingredient of most mining explosives and it is an essential ingredient of smokeless, so-called double base propellants. Attempts to nitrate glycerine experimentally were begun as long ago as 1830. Glycerine was dissolved in nitric acid without being cooled. The reaction therefore proceeded at a temperature distinctly higher than room temperature, and in these conditions glycerine did not undergo nitration but was oxidized, forming water-soluble hydroxy-keto-acids and hydroxy-acids. It was not until 1847 that nitroglycerine was obtained for the first time by Ascanio Sobrero [1] who used a nitration mixture of nitric and sulphuric acids at a low temperature. Afterwards the whole was poured into water. The oily nitroglycerine sank to the bottom, whence it could be readily separated and freed from acid by careful washing with water. Sobrero recognized the explosive properties of the new substance and named it pyroglycerine. However, although these properties engaged the attention of Sobrero he did not develop the appropriate application, for the danger of manufacturing and handling seemed likely to prohibit its use in practice.

Attempts to make use of nitroglycerine as a high explosive shell filling were carried out in various countries: in Russia they were done by Zinin and his co-worker Pietruszewski in 1854 [2]. However, the trials proved unsuccessful owing to the materials sensitiveness to shock.

The first important steps to develop the manufacture and application of nitroglycerine in mining were taken by a Swedish engineer—Alfred Nobel who learned about nitroglycerine from Zinin 1855, when residing in St. Petersburg [2a]. In 1862 a factory to produce "explosive oil" was built by Nobel in Helleneborg near Stockholm and in 1864–66 he was granted patents [3] for the method of nitrating glycerine by means of a mixed acid composed of nitric and sulphuric acid. At first nitroglycerine was separated from the spent acid by running off the whole into water; afterwards Nobel improved his method so as to get the nitration product as an individual phase.

In spite of numerous failures, as for instance the explosion of his factory in 1864, Nobel introduced the use of "explosive oil" in place of black powder (gunpowder) for mining purposes.

To initiate the nitroglycerine, detonators filled with black powder were used at first. Later, Nobel [4] invented blasting caps (detonators) charged with mercury fulminate for this purpose.

The liquid consistency of nitroglycerine and its sensitiveness to shock are great disadvantages in handling and transporting it.

Nobel endeavoured to diminish the sensitiveness of nitroglycerine to shock by dissolving it in methyl alcohol. The transport of such a solution proved markedly safer than that of nitroglycerine itself. On the spot, in the mine, this solution was treated with water and after decanting the upper aqueous–alcoholic layer above the nitroglycerine, which was precipitated in form of oil, the latter was used as a high explosive. However, this operation was troublesome. Based on an observation that a large quantity of nitroglycerine can be absorbed in diatomaceous earth (kieselguhr) to form a doughy mass, guhr dynamite, consisting of 75 parts by weight nitroglycerine and 25 parts kieselguhr was patented by Nobel in 1867 [5]. This new explosive rapidly become well known and popular. After 1868 about a dozen factories were established in various continents to manufacture nitroglycerine and dynamite.

The manufacture of nitroglycerine was also started in Russia by Pietruszewski, a co-worker of Zinin [2]. Intending to decrease the sensitiveness of nitroglycerine to shock, Pietruszewski mixed the explosive substance with a solid adsorbent, in this case magnesium carbonate. Since about 1867 nitroglycerine has been used in the Upper-Uspienskii district's gold mines in the Trans-Baykal of Siberia [6].

In 1875 Nobel [7] produced the so-called blasting gelatine by dissolving nitrocellulose in nitroglycerine. It is on the basis of this gelatine mixed with oxygen carriers, e.g. ammonium or sodium nitrates, that dynamites ("straight" dynamites) are produced at the present day. It was also Nobel who invented smokeless, "nitroglycerine" powder ("double base" powder), or so-called *ballistite* in 1888 [8]. Nitroglycerine has also found wide application as an ingredient of ammonium nitrate explosives for mining purposes.

The method of manufacturing nitroglycerine introduced by Nobel has been modified and improved. The research work of the authors listed below is cited as containing the most important achievements in this field: Nathan, Thomson and

Rintoul [9], A. Schmid [10], Raczyński [11], Biazzi [12]. A recent improvement in this field was developed in Swedish factory N. A. B. Gyttorp [13].

A broad review of the history of nitroglycerine and dynamite manufacture was published recently by Nauckhoff and Bergström [13].

PHYSICAL PROPERTIES

Nitroglycerine is an oily liquid and in pure form it is colourless and transparent. The commercial product is usually yellowish (of straw yellow colour) or pale brown depending on the purity of the original raw materials and on the conditions of manufacture. Nitroglycerine has a slight "sweetish" smell perceptible after heating to temperatures exceeding 50°C and it has a bitter-sweet and "burning" taste.

Freezing point

There are two modifications of nitroglycerine, differing in freezing point and crystalline forms. With respect to crystal structure the form melting at the lower temperature represents a labile form (Fig. 6) which can be transformed spontaneously into the higher melting stable form of nitroglycerine (Fig. 7).

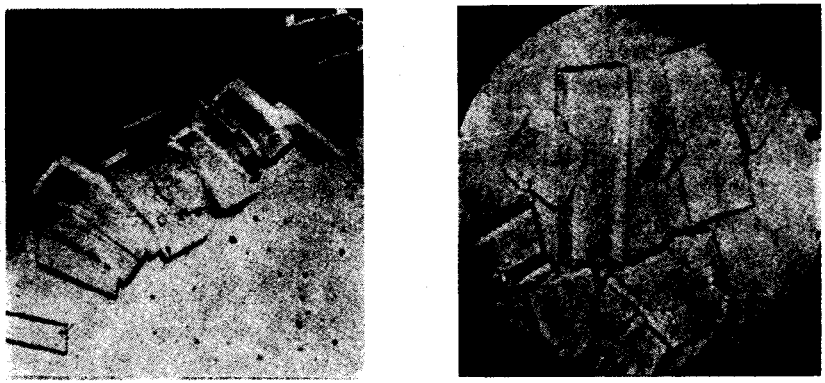


FIG. 6. Crystals of nitroglycerine, labile form (Hibbert [15]).

FIG. 7. Crystals of nitroglycerine, stable form (Hibbert [15]).

The freezing and melting temperatures of these transformations have been established by Kast [14] who also observed that very pure nitroglycerine is transformed on freezing mainly into the labile crystals, whereas a less pure sample often crystallizes in the stable form.

The conditions necessary for the formation of each crystal form were examined by Hibbert [15]. He found that if recently produced nitroglycerine is mixed with wood meal or pulverized glass and cooled to the temperature of −40°C, while being stirred vigorously, the labile form is produced. By introducing a crystal obtained in this way into another portion of cooled nitroglycerine, crystallization of the labile form can be induced.

On the other hand, if nitroglycerine is mixed with wood meal and sodium or ammonium nitrate under the same conditions the stable crystalline form is produced. Nitroglycerine which had been crystallized and afterwards melted readily solidifies again in the same crystalline form it possessed before melting*. However, if nitroglycerine is kept after melting for a longer period at a temperature exceeding 50°C, it is apt to become supercooled and to crystallize like a freshly prepared product again. Hibbert reported that the labile form of nitroglycerine is converted to the stable form after some 1–2 weeks' storage.

Hackel [17] has established that the transformation of the labile into the stable form does not proceed as readily as indicated by Hibbert. Thus, on keeping labile nitroglycerine for a period of 4 months in a thermostat at the temperature of 0°C no traces of conversion to the stable variant were observed. Further, Hackel did not confirm Hibbert's view that molten crystals of the stable form, seeded with labile crystals yielded crystals of the labile form which were unusually inclined to transform into the stable form. Simple, vigorous stirring would be enough to cause this conversion. The cardinal factor determining the stability of either form consists, according to Hackel, in safeguarding the nitroglycerine against being seeded with crystals of the other form.

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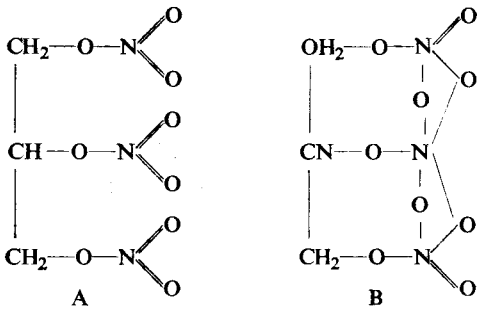
* The capacity of the molten nitroglycerine to crystallize again in its original form was proposed by Hibbert [16] as evidence for the supposition that both variants are isomers (A) and (B) differing in chemical structure:



Even if the disagreement of these chemical formulae with the accepted method of depicting the nitro group is disregarded, there is no evidence to confirm the existence of two such isomers.

Hackel has extended Hibbert's observations concerning the influence of certain substances on the formation of nitroglycerine crystals of different forms. Thus, adding urethane, phenylurethane, collodion, nitrocotton, cyclonite, tetryl, dinitrobenzene, or centralites I and II promotes the formation of the labile form. Admixtures of siliceous earth, trinitrobenzene, TNT, favour the creation of the stable form.

Freezing points for both variations of nitroglycerine, as published in different papers, are collected in Table 6.

TABLE 6

FREEZING TEMPERATURES OF NITROGLYCERINE MODIFICATIONS, °C

Modification	Nauckhoff [18]	Kast [14]	Hibbert [15]	Hackel [17]
Labile	–	2.1–2.2	1.9	1.9
Stable	12.4	13.2	13.0	13.0

Hibbert [15] assumed that the labile form of nitroglycerine belongs to the triclinic system, while according to Flink [19] the stable form has orthorhombic bipyramidal crystals.

On the basis of the dipole moment values and viscosity measurements of the two forms of nitroglycerine, de Kreuk [20] considered that the difference between the two forms is produced by rotational isomerism. According to this hypothesis the labile and stable forms would correspond to *cis*- and *trans*-isomers respectively. In a non-polar solvent the *trans* form predominates. In a polar solvent the content of the *cis* form increases and reaches a maximum in liquid nitroglycerine.

This can be seen from the figures for dipole moments in various solvents given below (p. 45).

The heat developed during the transformation of one form of nitroglycerine into the other is given on p. 46. The linear crystallization rate of nitroglycerine to form the stable modification at different temperatures was investigated by Nauckhoff [18] who found the following figures:

temperature, °C	rate, mm/min
+5	0.145
0	1.183
−5	0.267
−17	0.125

Solubility

Nitroglycerine is hardly miscible with water. One litre of water dissolves (according to Will [21], Naoúm [22] and Oehman [108]):

at 15°C	1.6 g nitroglycerine
20°C	1.8 g nitroglycerine
50°C	2.5 g nitroglycerine

The solubility of nitroglycerine in aqueous (1–10%) sodium carbonate is still lower (of the order of 1.0 g) [108].

Nitroglycerine is readily dissolved in most organic solvents and itself behaves as a good solvent. Thus, it is completely miscible in all proportions at room temperature with the following liquids: methyl alcohol, ethyl acetate, anhydrous acetic acid, benzene, toluene, xylenes, phenol, nitrobenzene, nitrotoluenes, pyridine, chloroform, dichloroethane, dichloroethylene, and the like.

Further, nitroglycerine can be blended in all proportions with other liquid nitric esters, such as methyl nitrate, the so-called nitroglycol—ethylene glycol dinitrate, diethylene glycol dinitrate, dinitroglycerine, trimethylolnitromethane trinitrate (nitroisobutylglycerine trinitrate), etc.

The solubility of nitroglycerine in halogeno derivatives of hydrocarbons depends on their chlorine content. Thus, nitroglycerine can be mixed with dichloroethylene in all proportions but with 100 parts of trichloroethylene at room temperature only 20 parts of nitroglycerine are miscible, whilst nitroglycerine dissolves with difficulty in tetrachloroethylene and pentachloroethane.

To an appreciable extent the solubility of nitroglycerine in ethyl alcohol depends on the temperature of the solvent and its water content. In the cold a limited quantity of nitroglycerine is dissolved in absolute alcohol, whereas at temperatures of about 50°C it mixes with absolute or 96% alcohol in all proportions. The solubility of nitroglycerine decreases as water is added to the ethanol. In consequence, when water is poured into an alcoholic solution, nitroglycerine is precipitated step by step. This precipitation becomes very considerable after the alcohol has been diluted from 50 to 25% concentration.

To characterize the solubility of nitroglycerine in ethyl alcohol the data quoted by Naoúm [22] are given below, in Table 7.

TABLE 7

THE SOLUBILITY OF NITROGLYCERINE IN ETHYL ALCOHOL

Ethyl alcohol	Temperature °C	Grammes nitroglycerine dissolved in 100 cm^3 ethyl alcohol
Absolute	0	*ca.* 30
Absolute	20	*ca.* 43
96%	20	31.6
50%	20	1.8
25%	20	0.7

Similarly other alcohols, such as propyl, isopropyl and amyl alcohols dissolve nitroglycerine at room temperature to a limited extent only. However, they are miscible in all proportions at 90–100°C.

In polyhydroxy alcohols nitroglycerine is still less soluble. The best of these solvents is ethylene glycol. Thus 100 g of ethylene glycol dissolve 12 and 20 g of nitroglycerine at 20 and 80°C respectively. The solubility of nitroglycerine in glycerol is very low.

For analytical purposes, attention must be paid to the solubility of nitroglycerine in acetic acid and in carbon disulphide, since these solvents can be used to separate nitroglycerine from aromatic nitro compounds. Thus nitroglycerine dissolves readily in 65% acetic acid which does not dissolve nitro compounds. In carbon disulphide, nitroglycerine dissolves with difficulty. At room temperature, 100 ml of this solvent dissolve about 1.25 g nitroglycerine. Nitro compounds, on the other hand, are readily dissolved in carbon disulphide.

Both in the cold and in the warm nitroglycerine is slightly soluble in aliphatic hydrocarbons, for example petrol, ligroine, kerosene, paraffin oil, lubricating oils, vaseline oil (Table 8).

TABLE 8

SOLUBILITY OF NITROGLYCERINE IN ALIPHATIC HYDROCARBONS (AFTER NAOÚM [22])

Solvent	Temperature °C	Grammes nitroglycerine dissolved in 100 g solvent
Ligroine	20	about 1.5
	80	about 6.0
Petrol	20	about 2
	80	about 6
Purified oil	20	about 4
	80	about 9

A comparatively high proportion of nitroglycerine can be blended with vegetable oils. For instance, at 20°C 100 g olive oil dissolve 20 g nitroglycerine and at 100°C about 25 g nitroglycerine are dissolved. Nitroglycerine is also relatively soluble in castor oil. Nitroglycerine is only very slightly soluble in an aqueous solution of ammonia, sodium hydroxide and potassium hydroxide. When hot it undergoes the process of hydrolysis (for more details see p. 7).

From the manufacturing point of view the solubility of nitroglycerine in sulphuric acid, nitric acid and in their mixtures is most important, hence great attention has been paid to this question.

Concentrated sulphuric acid readily dissolves nitroglycerine. It has been reported by Naoúm [22] that 100 g of 98% sulphuric acid at 20°C dissolve about 26 g nitroglycerine and 100 g of 70–80% sulphuric acid are capable of dissolving 7.5 g of nitroglycerine.

In the presence of concentrated sulphuric acid, nitroglycerine is hydrolysed to form HNO_3. According to the concentration of the sulphuric acid the products are either esters containing a smaller number of nitrate groups or mixed esters of nitric and sulphuric acids, for instance glyceryl–sulphuric nitrates. At room temperature anhydrous nitric acid mixes with nitroglycerine in all proportions. The solubility decreases step by step as the concentration of acid is diminished. Thus a 100 g portion of 65% nitric acid at 20°C dissolves 8 g nitroglycerine. Solutions of nitro-

glycerine in nitric acid are unstable since on storage they begin to decompose as a result of oxidation caused by the nitric acid, and nitric oxides are evolved.

Nathan and Rintoul [23], when studying the solubility of nitroglycerine in mixed acids, found that compositions with the ratio $H_2O : HNO_3 = 1.1$ and sulphuric acid content from 0 to 60% are particularly dangerous in this respect: they readily produce an uncontrollable reaction, and no acid of a composition in or near this zone should ever be allowed to come in contact with nitroglycerine in a manufacturing operation. This extremely important observation was recently studied in detail by Oehman *et al.* [110], (see Fig. 26, p. 84).

Nathan and Rintoul also examined the solubility of nitroglycerine in acid mixtures with $H_2SO_4 : H_2O$ and $H_2SO_4 : HNO_3$ ratios having the constant values: 5.8 and 10.4 respectively.

Their figures were used by Pascal [24] to construct a triangular diagram—Fig. 8 (Table 9).

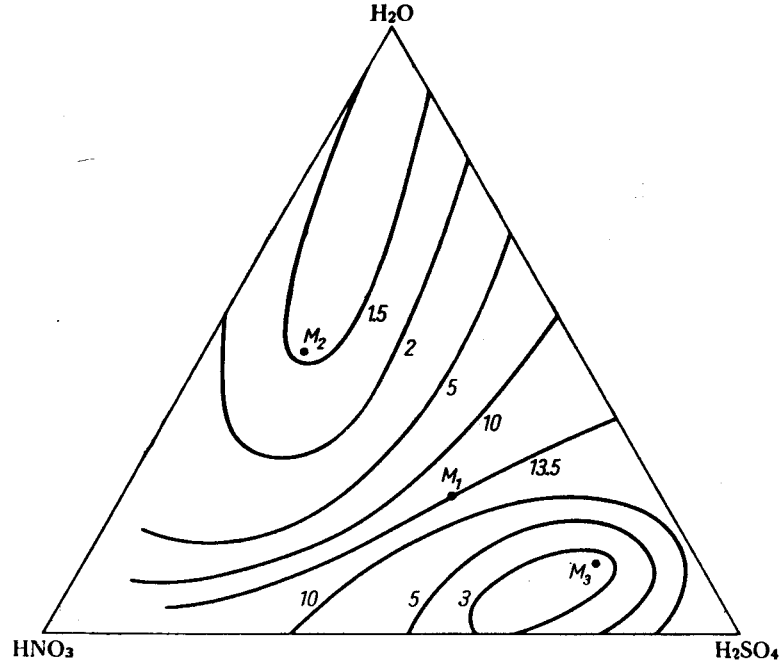


FIG. 8. Solubility (in %) of nitroglycerine in mixtures of nitric acid, sulphuric acid and water, according to Pascal [24].

TABLE 9

SOLUBILITY OF NITROGLYCERINE IN MIXTURES OF HNO_3 AND H_2SO_4

Designation of mixture	Composition of mixture, %			Quantity of dissolved nitroglycerine, %
	HNO_3	H_2SO_4	H_2O	
M_1	24	50	26	13.5
M_2	38	20	42	1.6
M_3	13	75	12	2.5

More recently investigations of the solubility of nitroglycerine in mixed acids (spent acids) have been made by Oehman [108], Klassen and Humphrys [25] (Fig. 9).

In practice the nitrating conditions most frequently applied are those which permit the composition of the spent acids after nitration to approximate to the mixture M_3.

Naoúm [22] has established the solubility of nitroglycerine in mixed acids composed of ingredients resembling approximately the mixture M_3 (Table 10).

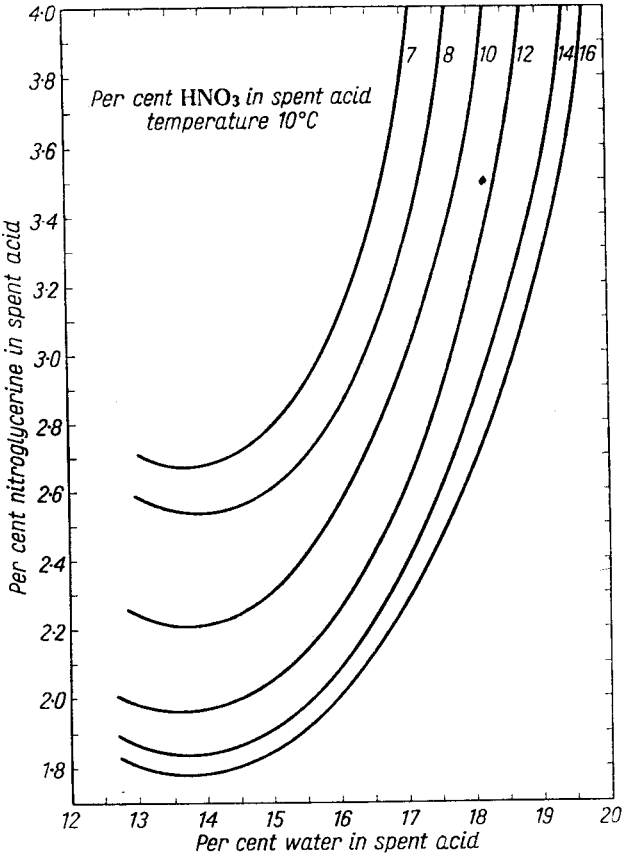


FIG. 9. Solubility of nitroglycerine in spent acid, according to Klassen and Humphrys [25].

TABLE 10

SOLUBILITY OF NITROGLYCERINE IN MIXTURES OF HNO_3 AND H_2SO_4

Composition of mixture, %	I	II	III	IV	V	VI
Nitric acid, HNO_3	10	10	10	15	15	15
Sulphuric acid, H_2SO_4	70	75	80	80	75	75
Water, H_2O	20	15	10	5	10	15
Quantity of nitroglycerine soluble in 100 parts by weight of mixed acid	6.00	3.55	3.33	4.37	2.60	2.36

Part of the nitroglycerine dissolved in this mixture of acids undergoes hydrolysis.

Concentrated hydrochloric acid does not dissolve nitroglycerine. On heating, a gradual decomposition occurs accompanied by a dark yellow colour due to hydrolysis and the production of nitrosyl chloride.

Nitroglycerine as a solvent. The capacity of nitroglycerine to dissolve aromatic nitro compounds has been studied for its practical importance, since blends of nitroglycerine with nitro compounds often form the base components of high explosives, as for example dynamites and smokeless powders. Investigating systems which contain nitroglycerine makes it possible for instance to find substances which decrease the freezing point of nitroglycerine. The first experiments of this kind were performed by Mikołajczak [26]. In order to lower the freezing point of nitroglycerine, dinitroglycerine was added. Afterwards Herlin [27] investigated the effect of adding nitro compounds. The influence of nitroglycol, dinitrochlorohydrin, and diglycerol tetranitrate was determined by Sapozhnikov and Snitko [28].

Hackel [29] carried out extensive research by means of thermal analysis to establish the eutectic composition of both the labile and stable modification of nitroglycerine with aromatic nitro compounds and with substances used in manufacturing smokeless powders such as centralites, urethanes and others listed in Table 11 and Fig. 10.

TABLE 11

COMPOSITION OF EUTECTICS FORMED FROM NITROGLYCERINE

	Stable form		Labile form	
	Nitro-glycerine percentage in eutectic	Freezing temperature of eutectic °C	Nitro-glycerine percentage in eutectic	Freezing temperature of eutectic °C
Nitrobenzene	45.5	−15.2	57.5	−22.9
m-Dinitrobenzene	82.5	5.0	88.0	− 5.4
2,4-Dinitrotoluene	72.7	6.1	89.0	− 4.1
2,4,6-Trinitrotoluene	82.9	6.3	90.0	− 4.0
Tetryl	90.0	9.8	94.0	− 0.6
Cyclonite	99.5	12.3	99.7	1.2
Nitroglycol	*ca.* 20	*ca.* −30	*ca.* 40	*ca.* −40
Pentaerythritol tetranitrate	98.5	12.3	98.9	1.3
Phenyl urethane	90.0	9.6	93.0	− 0.8
Phthalide	76.5	0.8	8.10	− 8.2
Methyl centralite	96.5	10.6	98.0	0.8
Diphenylamine	93.0	9.8	96.0	− 0.4

The freezing points of blends of nitroglycerine and nitroglycol have been investigated by Avogadro di Cerrione [30] who established experimentally that both substances can be dissolved in any quantitative ratio to form the following eutectic mixtures:

(1) 29% stable form of nitroglycerine,
71% nitroglycol,
melting point −29°C;
(2) 39% labile form of nitroglycerine,
61% nitroglycol,
melting point −23°C.

Nitroglycerine is able to dissolve nitrocellulose containing a comparatively low percentage of nitrogen, namely collodion cotton ("soluble nitrocellulose"). Solution takes place slowly at room temperature, whereas at 60–65°C it is complete in some 15–20 min. The consistency of the solution obtained depends on the concentration of nitrocellulose in the nitroglycerine and on the viscosity of the nitrocellulose. For practical purposes, for instance, in the manufacture of blasting gelatine, collodion cotton that gives high viscosity solutions of jelly consistency should be used even if they contain only a small quantity of nitrocellulose.

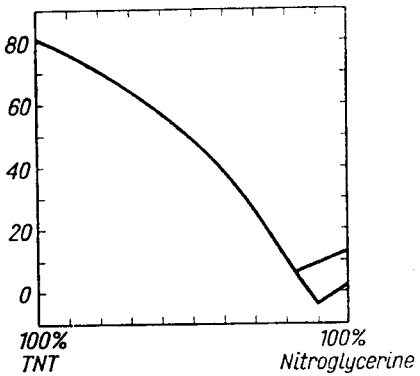


FIG. 10. Eutectic of nitroglycerine with TNT (Hackel [17]).

Nitroglycerine can also dissolve a certain amount of inorganic acid. It has been established by Wallerius [31] that the higher the concentration of nitric acid in the spent acid, the higher is the residue of nitric acid in the nitroglycerine after it has been separated. If for instance the HNO_3 concentration in the spent acid amounts 10% then the quantity of HNO_3 left in the nitroglycerine amounts to 6.15%. A concentration of nitric acid in the spent acid amounting to 14% corresponds with as much as 8.6% of HNO_3 retained in the nitroglycerine. As for the content of sulphuric acid in the nitroglycerine, it remains the same in both cases and amounts only to 0.3% of H_2SO_4. According to Oehman [32] the acid (unwashed) nitroglycerine contains about 8% of nitric acid; of the sulphuric acid it contains, 0.1% is dissolved and 0.5% is emulsified.

In the system nitric acid–nitroglycerine–water, a labile equilibrium is established, determined by the coefficient of phase separation. Thus under certain conditions as much as 8% nitric acid passes into the water phase whereas the nitroglycerine does not contain more than 0.01% HNO_3. A thorough study of the partition of HNO_3 and dinitroglycerine between nitroglycerine and aqueous solutions was made by Oehman [108].

These data are very important for practical purposes, namely for the problem of purifying nitroglycerine by washing. This problem is discussed in detail later (see p. 74).

Very recently Ropuszyński [33] has proved that nitrating glycerine at an elevated temperature exerts a propitious influence upon the stability of the product. This is due to the fact that nitroglycerine obtained at a higher temperature before being stabilized by the usual methods i.e. is washed by means of water and of sodium carbonate solution, contains less residual acid.

The data in question are collected in Table 12.

TABLE 12

THE RELATION BETWEEN THE NITRATING TEMPERATURE AND RESIDUAL ACID CONTENT

Nitrating temperature °C	Residual acid content		Heat test min
	$\%HNO_3$	$\%H_2SO_4$	
15	0.0132	0.0024	15
25	0.0057	0.0017	24
40	0.0052	0.0008	30

Boiling point and vapour pressure

Nitroglycerine begins to boil at a temperature above 180°C. At the same time decomposition takes place accompanied by the evolution of nitric oxides and water vapour. In the distillate, dilute nitric acid and some nitroglycerine is present, probably carried over with the water vapour. The water is formed as a result of the partial decomposition of nitroglycerine which occurs when it is heated to high temperature (see. p. 47).

Owing to decomposition, it is impossible to determine the precise boiling point, though Belayev and Yuzefovich [34] reported that at a pressure of 50 mm Hg the boiling point of nitroglycerine is 180°C, whereas under a pressure of 2 mm Hg it is 125°C.

For the vapour pressure of nitroglycerine different data are to be found in the literature which are incompatible and depend to an appreciable extent upon the method of measurement chosen. Thus the vapour pressure of nitroglycerine at 25°C was found by Chiaraviglio and Corbino [35] to be below 0.00012 mm Hg.

The values found by Marshall and Peace [36] are of the same order:

at 20°C	0.00025 mm Hg	at 60°C	0.0188 mm Hg
30°C	0.00038 mm Hg	70°C	0.043 mm Hg
40°C	0.0024 mm Hg	80°C	0.098 mm Hg
50°C	0.0072 mm Hg	93.3°C	0.29 mm Hg

Naoúm and Meyer [37], on the other hand, published significantly higher figures.

By means of the dynamic method they found the following data:

at 20°C 0.011 mm Hg
at 60°C 0.036 mm Hg

Applying the statistical method they have calculated that at 20°C the vapour pressure of nitroglycerine is 0.0009 mm Hg.

According to Rinkenbach [38] the vapour pressure of nitroglycerine is:

at 20°C 0.0015 mm Hg
at 60°C 0.060 mm Hg

The vapour pressure of nitroglycerine has also been determined by Crater [39] and Brandner [40]. The latter attempted to remove the discrepancies which exist between the values published by different investigators. Thus the data of Brandner are:

temperature, °C	pressure, mm Hg
30	0.0012
35	0.0020
40	0.0030
45	0.0047
50	0.0081

The results of these researches are not in line with the data found by Naoúm and Meyer, nor with those of Crater. These differences seem to be explicable by suggesting that Naoúm, Meyer and Crater did not use absolutely dry nitroglycerine. The data of Brandner approximate to the results quoted by Rinkenbach [38] and Marshall and Peace [36] (at higher temperatures).

Using the Marshall data, Roginskii and L. M. Sapozhnikov [41] calculated the heat of evaporation of nitroglycerine ΔH_v to be:

at $T = 100°K$ 20.64 kcal/mole
at $T = 140°K$ 20.38 kcal/mole
at $T = 180°K$ 20.11 kcal/mole

Using his own data, Brandner has calculated the heat of evaporation of nitroglycerine to be $\Delta H_v = 19.17$ kcal/mole. The same author has investigated the vapour pressure of nitroglycol (see p. 143) and calculated that of nitroglycerine–nitroglycol mixed solutions. The results are collected in Table 13.

TABLE 13

VAPOUR PRESSURE OF THE NITROGLYCERINE–NITROGLYCOL BLENDS

Percentage of nitroglycol	Total vapour pressure, mm Hg			
	10°C	30°C	40°C	50°C
10	0.0027	0.186	0.0433	0.1002
20	0.0051	0.0345	0.1159	0.1841
40	0.0093	0.0624	0.1475	0.3314

Häussermann [42] reported that a small quantity of nitroglycerine distils with steam. With the saturated steam produced from 1 l. of water, 8 g of nitroglycerine are carried over at a temperature of 100°C.

Naoúm [22] reported that on exposure of a 20-g sample of nitroglycerine on a 70 mm dia. watch glass for a period of 24 hr the following weight decrease occurred:

at 50°C	0.04 g (0.2%)
at 75°C	0.32 g (1.6%)
at 100°C	about 2 g (about 10%)

In agreement with reports of Rinkenbach [38] the weight loss of a nitroglycerine specimen at a temperature of 60°C amounts 0.11 mg/cm^2/hr.

Specific gravity and other physical constants

According to Perkin [43] the specific gravity of nitroglycerine is:

at 4°C	1.614 g/cm^3
at 15°C	1.600 g/cm^3
at 25°C	1.591 g/cm^3

Kast determined the value as 1.5995 g/cm^3 at a temperature of 15°C.

On freezing nitroglycerine contracts in volume by as much as 8.3%. The specific gravity of the stable modification at 10°C is 1.735 g/cm^3 (Beckerhinn, [44]).

The refractive index of nitroglycerine is $n_D^{20} = 1.4732$.

The viscosity of nitroglycerine is higher than that of water but many times less than that of glycerine. The following results have been published by Naoúm:

The time of discharge from a 20-ml pipette is 6 sec for water, 15 sec for nitroglycerine, and 540 sec for glycerine.

According to de Kreuk [20] the viscosity of nitroglycerine at 20°C is 37.8 cP. Rinkenbach [38] gives the figure 35.5 cP. See also Table 3 (p. 3).

Dielectric constant $\varepsilon_{20} = 19.25$ and dipole moments μ of nitroglycerine were determined by de Kreuk [20]:

nitroglycerine (pure, liquid)	$\mu = 3.82$ D
nitroglycerine in hexane	$\mu = 2.56$ D
nitroglycerine in carbon tetrachloride	$\mu = 2.88$ D
nitroglycerine in benzene	$\mu = 3.16$ D

According to this author different values of μ are due to rotational isomers present in various proportions. Solutions in non-polar solvents would contain a high proportion of *trans*-isomer, whose dipole moment is very low.

Absorption spectra

T. Urbański and Witanowski [109] found that the infra-red absorption spectrum contains the bands:

NO_2 asymmetrical stretching vibrations: 1675, 1654, 1645 cm^{-1}
NO_2 symmetrical stretching vibrations: 1293, 1276 cm^{-1}

Various frequencies are most likely due to rotational isomers (see above).

THERMOCHEMICAL PROPERTIES

The specific heat of nitroglycerine was determined by Nauckhoff [18] as 0.356 cal/g and that of the crystalline substance (stable form) as 0.315 cal/g. For liquid nitroglycerine Belayev [45] published the value 0.4 cal/g.

The heat of crystallization (freezing) of nitroglycerine has been determined by many authors (Nauckhoff [18], Beckerhinn [44]). The most complete investigations were those performed by Hibbert and Fuller [46] who have established the following data:

heat of crystallization of the stable form 33.2 cal/g
heat of crystallization of the labile form 5.2 cal/g

Hence, the heat of transforming the labile variation into the stable one is 28 cal/g.

Heat of combustion and heat of formation of nitroglycerine. It has been reported by Rinkenbach [47] that the heat of combustion $-\Delta H_c$ at constant volume should be 368.4 kcal/mole, which corresponds to 1623 kcal/kg. Thus the heat of formation $-\Delta H_f$ is+85.3 kcal/mole (+374 kcal/kg).

Values for the heat of formation of nitroglycerine published by other authors are listed below:

415 kcal/kg (Brunswig [48])
416 kcal/kg (Kast [49])
370 kcal/kg (J. Taylor and Hall [50])

According to information from different sources the heat of nitration of glycerol to nitroglycerine varies from 120 to 170 kcal per 1 kg of glycerine.

CHEMICAL PROPERTIES

In the presence of reducing agents such as tin and hydrochloric acid, zinc and acetic acid, alkaline sulphides and hydrosulphides, nitroglycerine is reduced to form glycerine and ammonia. This is evidence that there are no nitro groups attached directly to a carbon atom, otherwise amines would be obtained. Like every ester, nitroglycerine undergoes the reaction of hydrolysis. On heating in a solution of sodium or potassium hydroxide in water or alcohol, not only is the hydrolytic process stimulated, but also oxidation and reduction processes accompanied by the formation of organic acids and of nitrates and nitrites. In consequence the reaction products are more complicated than might be expected. According to Hay [51, 52] the reaction proceeds according to eqn. (2), p. 7.

This equation does not comprise the whole complex of simultaneous chemical reactions, which have already been discussed (p. 7). Later investigators (Vignon and Bay [53]; Silberrad and Farmer [54], Berl and Delpy [55]) also found such products as aldehyde resins, oxalic acid and ammonia. It is characteristic that from nitroglycerine hydrolysed in an alkaline medium no glycerine is recovered. Glycerine can however be obtained again when the hydrolysis is carried out in the presence

of readily oxidizable substances. Thus it was established by Klason and Carlson [56] that as a result of hydrolysing nitroglycerine by means of NaOH in the presence of phenyl mercaptan, glycerine was produced together with diphenyl sulphide.

The action of concentrated sulphuric acid and the formation of mixed sulphuric–nitric esters, as well as the action of nitric acid and mixtures of nitric–sulphuric acid and water and of hydrochloric acid have been discussed above. Concentrated hydriodic acid of 1.5 density decomposes nitroglycerine to glycerol and nitric oxides.

Dimethyldiphenyl urea ("Carbamite") and nitroglycerine form a non-homogenously melting addition product of 1:1 molecular composition according to Hackel [29].

STABILITY

Heating nitroglycerine (particularly moist samples) at a temperature of 75°C brings about an apparent decomposition within 3–4 days characterized by the development of acid products. After 6 days the presence of HNO_3 is clearly distinguishable. If the volatile products of decomposition are removed, e.g. by blowing with air, as quickly as they are developed, then only very slow decomposition of the nitroglycerine takes place.

Nitroglycerine contaminated with acid as the result of insufficient washing or due to thermal decomposition undergoes decomposition. Small samples undergo gentle decomposition to produce oxides of nitrogen, nitric acid and organic acids, including among others oxalic acid. Naoúm reported that 10 g of nitroglycerine decomposed to form 2 g of oxalic acid and 2.3 g of other crystalline acids and oxidation products. The products are slightly different if the specimen to be decomposed is kept at a temperature higher than 50°C. The residue is a viscous syrup containing glyceric acid and other organic acids. A valuable investigation into the relation between the composition of spent acid and the stability of nitroglycerine was recently carried out by Oehman *et al.* [110] (Fig. 26, p. 84).

Decomposition of small unconfined samples of nitroglycerine is not dangerous. On confinement, however, the reaction takes a different course, since as decomposition proceeds increasing quantities of gaseous reaction products cause a high pressure to develop and this stimulates further decomposition of the nitroglycerine. The decomposition of large quantities of nitroglycerine can be dangerous. Eventually the heat caused by decomposition is not removed quickly enough and an explosion may take place. It has been proved by Roginskii [57] that such an explosion is not necessarily due to the elevation of temperature to the point of initiation (i.e. to a temperature over 180°C). Slow decomposition at a lower temperature in the presence of the nitric acid, which exerts a catalytic effect, is accompanied by development of branched reaction chains and an explosion can occur. Owing to this an explosion is possible even at a temperature considerably lower than 180°C.

Test specimens of 0.3 g nitroglycerine with an admixture of 5% HNO_3 in sealed ampoules were kept by Roginskii in a thermostat at a temperature of 41°C. Explosion

took place after an interval of 320 min, by which time the temperature of the sample exceeded that of the thermostat by only a few centigrade degrees (Fig. 11).

The decomposition of nitroglycerine is also accelerated in the presence of other substances produced during the course of reaction. Attention was paid to that phenomenon by several earlier authors, like e.g. Sapozhnikov [58]. It has been confirmed by more recent investigations. For instance Lukin [59] has established

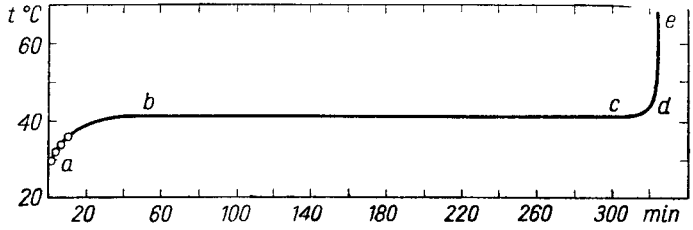


FIG. 11. Decomposition of nitroglycerine with 5% HNO_3 at 41°C according to Roginskii [57]: *ab*—warming up the sample in a thermostate, *cde*—self heating of the sample, *e*—point of explosion.

that the chief accelerating agents are NO_2 and water. Nitrogen, NO, CO and CO_2, on the other hand, exert no accelerating effect. Andreyev *et al.* [60] have shown that water has the same influence upon nitroglycol.

According to results obtained by Andreyev and Bezpalov [61] dry nitroglycerine starts to undergo an autocatalytic decomposition after having been heated for a period of 40 hr at 100°C, whilst with nitroglycerine containing 0.01% of water the interval is shortened to 30 hr. In the presence of 1.5% water the time is as short as 2 hr.

R. Robertson [62] examined the decomposition of nitroglycerine at temperatures from 90 to 135°C, using a carbon dioxide stream to remove volatile decomposition products. The concentration of nitrogen oxides in the jet of carbon dioxide was established spectrographically. He found in this way that nitroglycerine decomposed in a manner similar to that of fairly well stabilized nitrocellulose, but more rapidly. In the temperature range of 95–125°C, every 5° elevation of temperature doubled the decomposition rate in these conditions.

T. Urbański, Kwiatkowski and Miładowski [63] examined the decomposition of nitroglycerine at 110°C and found the following figures for the pH of the aqueous extracts (Table 14):

TABLE 14

Samples	pH after heating at 100°C for		
	1 hr	2 hr	3 hr
2.0 g	3.05	2.77	2.57
2.5 g	2.94	2.70	2.45

The characteristic shape of the curve of pH as a function of time is given in Fig. 12.

Addition of nitro compounds (such as nitro derivatives of benzene and toluene) neither changes the pH nor the shape of the curve.

The decomposition of nitroglycerine at higher temperatures was investigated by Snelling and Storm [64] who established that at a temperature of 135°C the decomposition is sharply distinct from the lower temperature decomposition and

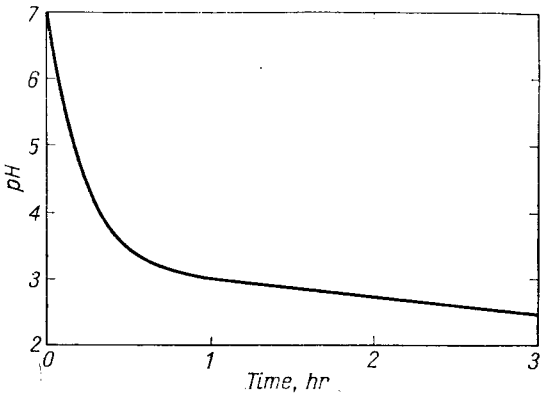


FIG. 12. Change of pH of aqueous extract of nitroglycerine heated at 110°C (T. Urbański, Kwiatkowski, Miładowski [63]).

the substance becomes red coloured owing to absorption of the decomposition products. At 145°C decomposition is accompanied by development of gaseous products and becomes very energetic. At 165°C the process is still more vigorous: dilute nitric acid and glycerol nitrates are distilled simultaneously. The remainder is a liquid containing glycerol, its mono- and dinitrates as well as other products difficult to identify. At a temperature of 180–185°C the nitroglycerine becomes highly viscous and at 215–218°C detonation occurs.

Temperature of initiation of nitroglycerine is 200–205°C (bath temperature), the rate of the temperature increase being 20° per min. Above 180°C a distinct exothermic decomposition of the substance begins, and hence at the moment of explosion the temperature of the nitroglycerine is higher than that of the bath, i.e. 215–218°C (Snelling and Storm [64]).

The behaviour of nitroglycerine on a heated metallic surface has been studied by T. Urbański and Rychter [65]. A drop of nitroglycerine allowed to fall on a metal plate heated to a temperature between 215 and 250°C exploded with violence to deform the plate. These observations suggest that the phenomenon is to be regarded as detonation or an effect resembling detonation. If the plate is heated to a temperature exceeding 420°C the drop of nitroglycerine acquires a spherical form and burns gently. At 470°C the slowest burning, lasting 2.0 sec, was observed.

This phenomenon is illustrated in Fig. 13.

The activation energy E needed for the thermal decomposition of nitroglycerine was calculated by T. Urbański and Rychter to be:

for temperature ranging from 215 to 250°C $E = 37.40$ kcal/mole
at temperatures over 470°C $E = 4.975$ kcal/mole

The first of those values is of the same order as those obtained by other authors. Thus considering the numeral data of Robertson [62] and Will [66] the following values of the activation energy necessary to decompose nitroglycerine were reported by Semenov [67]:

150–190°C $E = 50.0$ kcal/mole
125–150°C $E = 45.0$ kcal/mole
20–125°C $E = 42.6$ kcal/mole

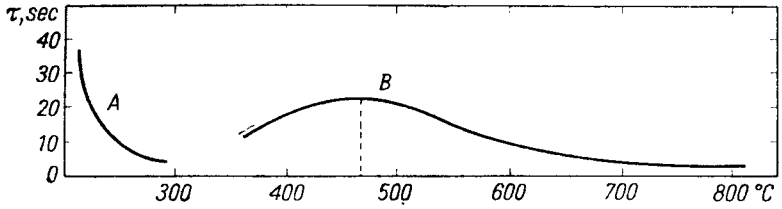


FIG. 13. Decomposition of nitroglycerine on a hot metal plate: A—violent decomposition, B—quiet decomposition of spheroid (T. Urbański and Rychter [65]).

Attention was drawn by Semenov to the fact that explosive substances are characterized by a high value of the activation energy E, as well as of the temperature-independent factor B.

This has been confirmed in a recent reports by Andreyev, Glaskova, Maurina and Svetlov [60]. According to these authors the activation energy of nitroglycerine decomposition at 140–150°C is $E = 45.0$ kcal/mole ($\log_{10} B = 20$).

It follows from the calculations of T. Urbański and Rychter that a non-explosive decomposition of nitroglycerine is characterized by a low E value which agrees with the above considerations of Semenov.

The ability of nitroglycerine to decompose readily when heated to a relatively low temperature (from 50°C upwards) long ago aroused suspicions that the chemical stability of this substance is low and that in the course of time it gradually undergoes spontaneous decomposition at room temperature. Well purified nitroglycerine, however, does not undergo decomposition during storage as has been realized from many years experience. Thus for instance, a sample of nitroglycerine obtained by Sobrero in 1847, preserved in the factory at Avigliana for over 70 years and regularly examined in the laboratory there has shown no signs of any change in stability. At 1912 a bore hole filled with nitroglycerine was found in a Swedish mine which had not been worked for a 38 years. The hole was a relic from the time when nitroglycerine was used alone as "blasting oil". The average annual temperature in this area is +8°C yet no changes in properties have been established in the nitroglycerine [22].

It was also noted that samples of blasting gelatine and dynamite which had been manufactured in Europe and delivered to Africa, and then sent back to Europe after several years showed no marks of decomposition [22]. Actually it is now agreed that very pure nitroglycerine is sufficiently stable at a temperature corresponding to the mean climatic temperature experienced in Europe. However, it should be protected from higher temperatures, and those approaching 50°C must be considered as dangerous. Nitroglycerine which has been heated to this temperature should be carefully checked. Similarly nitroglycerine which has been exposed to a direct sunlight should be tested (see below).

In this connection special attention should be paid to the control of nitroglycerine purity by means of the heat test (also called Abel test) which was described earlier (p. 23).

In the U.S.A. and some other countries an examination of the acidity of nitroglycerine by means of litmus paper is obligatory as well in addition to the Abel test.

The action of light. The opinion is expressed in the literature (e.g. Naoúm [22]) that diffused daylight has no adverse effect on nitroglycerine. Nevertheless in plants manufacturing or using nitroglycerine the latter is protected from direct sunlight.

T. Urbański, Malendowicz and Dybowicz [68] examined the behaviour of nitroglycerine (and of other nitric esters) exposed to ultra-violet rays and established that nitroglycerine irradiated once for a short period with a quartz lamp started to undergo slow decomposition which stopped only after an interval of 2–3 days. A sample of 3 g nitroglycerine was irradiated for 1 hr with rays from quartz lamp passing through a filter permeable to rays of 3200–4100 Å whilst maintained at a temperature of 15°C. In order to test the decomposition of the specimen, from time to time 0.25–0.5 g sample of the substance were removed, shaken with water and the pH values determined. The following results have been obtained: immediately after irradiation pH = 6.86; after 6, 24, 48 and 72 hr—6.12, 4.66, 4.48 and 5.22 respectively.

The decomposition of a sample irradiated for 10 min without any filter was similar.

By means of the Taliani–Goujon stability test it has been demonstrated that nitroglycerine which has previously been irradiated decomposes distinctly more quickly than non-irradiated nitroglycerine.

According to experiments by Deb [69] explosion of nitroglycerine can be provoked by intensive irradiation with ultra-violet rays (of 900 J strength), if the substance was previously heated to 100°C.

Kaufman [111] found that nitroglycerine is quite susceptible to γ-radiation, N_2, nitrogen oxides, H_2, CO_2 and CO being evolved.

EXPLOSIVE PROPERTIES

The explosive decomposition of nitroglycerine is generally expressed by the following equation:

$$4C_3H_5(ONO_2)_3 \longrightarrow 12CO_2 + 10H_2O + 6N_2 + O_2 \qquad (2)$$

According to Naoúm's [22] calculations the heat of explosion ought to amount in this case to 1485 kcal/kg, the volume of gases $V_0 = 715.7$ l./kg (or after condensation of water 469 l./kg), the temperature 3185°C (this number is repeated by the author after Hess [70]); thence the "force" $f = 9292$ m.

It has been established experimentally by Sarrau and Vieille [71] that the volume of gases, after the water vapour had been condensed, is 465 l./kg, i.e. a value very close to the value obtained by calculation. However, the composition of the gases found by these authors is different, probably in consequence of the incomplete explosive decomposition of nitroglycerine under the conditions of the experiment (calorimeter bomb).

After condensation of water vapour, the following composition has been established for the gases:

CO	35.9%
CO_2	12.8%
NO	48.2%
N_2	1.3%
H_2	1.6%
CH_4	0.2%

As reported by Bowden and Yoffe [72] the composition of the gaseous products evolved during explosion of nitroglycerine depends on the method of initiating the substance (composition of products in per cent):

	NO	N_2O	N_2	CO_2	CO	H_2	O_2
Initiated by detonation	—	—	32.0	63.1	—	—	4.9
Initiated by shock	29.7	2.3	11.7	28.8	25.5	5.0	—
Initiated by heating to 180°C	50.3	1.0	2.1	17.2	28.9	0.5	—

A different equation for the decomposition of nitroglycerine based partly on the data of Sarrau and Vieille [71] and partly on his own experiments was published by Kast [49]

$$32C_3H_5(ONO_2)_3 \longrightarrow 96CO_2 + 80H_2O + 6NO + 45N_2 + 5O_2 \qquad (3)$$

together with the following figures: heat of explosion 1455 kcal/kg, volume of gases $V = 715$ l./kg, temperature 4250°C, "force" $f = 12{,}240$ m.

Other sources quote the values listed below (heat of formation—see p. 46):

heat of explosion	temperature
1470 kcal/kg (Escales [73])	3153°C (Gody [75])
1478 kcal/kg (Berthelot [74])	3005°C (Wuich [76])

Sensitiveness to shock. It was Nobel [77] who first established in 1869 that crystalline nitroglycerine is significantly less sensitive to shock than the liquid. Advantage was taken of this property (Mowbrey [78]), in transport. The sensitiveness of nitro-

glycerine has been examined in detail by Hackel [17]. He found that the stable modification was slightly more sensitive than the labile form. The results of his experiments are collected below:

liquid nitroglycerine gives	10% explosions due to a shock of 0.08 kgm/cm^2
	50% explosions due to a shock of 0.11 kgm/cm^2
crystalline nitroglycerine, stable form	10% explosions due to a shock of 0.51 kgm/cm^2
	50% explosions due to a shock of 0.65 kgm/cm^2
crystalline nitroglycerine, labile form	10% explosions due to a shock of 0.63 kgm/cm^2
	50% explosions due to a shock of 0.78 kgm/cm^2

In the earlier experiments of Beckerhinn [79], Hess [70] and Will [80] it was reported that in order to bring about an explosion of solid nitroglycerine a 3–4 times more powerful shock was needed than in the case of liquid nitroglycerine.

Cronquist [81] has found that a mixture containing both liquid and crystalline nitroglycerine is more sensitive to shock than either of them alone. This is thought to be the result of friction between the sensitive liquid and the crystals. Nitroglycerine readily explodes on impact with a rifle bullet.

Although nitroglycerine is very sensitive to shock and explodes readily if stimulated in various ways—both mechanical and thermal, it can often undergo incomplete explosion.

The following data for nitroglycerine for the net expansion in the lead block (with water tamping), obtained when detonators of different initiating strength were used, have been reported by Naoúm [22]:

detonator No. 1	190 cm^3
detonator No. 2	225 cm^3
detonator No. 6	460 cm^3
detonator No. 8	590 cm^3

In these experiments, Naoúm showed that weak initiation with the No. 1 detonator produced only 32% of the effect obtainable by means of the No. 8 detonator. Nitroglycol and methyl nitrate explode more completely even if initiated with weak initiation differing in this respect from nitroglycerine.

A certain difficulty in detonating nitroglycerine is to some extent explicable by its high viscosity and the fact that it is a liquid. If on the other hand nitroglycerine is mixed with diatomaceous earth in the ratio of 75 parts of nitroglycerine to 25 parts of kieselguhr the detonating capacity of nitroglycerine is increased. Under these conditions on initiation with a No. 1 detonator the expansion recorded in the lead block test is 285 cm^3, whilst with a No. 8 detonator it is 305 cm^3. The insignificant difference between these two values is due to the difference in the detonation strength of the initiators themselves and if a correction is applied, the values are approximately the same. Undoubtedly both the dispersion of the nitroglycerine over a large surface area on the particles of kieselguhr and its extensive contact with air contained in the absorbent facilitate explosion.

These considerations would suggest that solid nitroglycerine is likely to explode more readily than the liquid nitroglycerine as, indeed, it does, as confirmed experimentally by Gorst and Andreyev [82] and by Hackel [29]. The results of Hackel's investigations are quoted in Table 15.

TABLE 15

THE LEAD BLOCK EXPANSION* BROUGHT ABOUT BY DETONATION OF NITROGLYCERINE

Type of nitroglycerine	Sand tamping cm^3	Water tamping (with admixture of glycerine) cm^3
Crystalline nitroglycerine (both modifications)	390	630
Liquid nitroglycerine	390	510

* The experiments were performed with blocks cooled to a temperature between −2 and −5°C. This is why the resultant values are lower when compared with the data quoted by other authors.

Sensitiveness to friction. Nitroglycerine is sensitive to friction. Thus, for instance, an explosion can take place simply as the result of rubbing it in a porcelain mortar with a rough surface.

Rate of detonation. The rate of explosion of a liquid explosive may vary within wide limits. Thus, according to numerous experiments it has been established that for liquid nitroglycerine the order of the explosion rate is 1000–8000 m/sec. The detonation rate of solid nitroglycerine, on the other side, does not vary in this way. It amounts 8000 m/sec at the maximum density of loading.

The explosion rates of liquid and crystalline nitroglycerine found by different authors are collected in Tables 16 and 17.

It follows from the data quoted that liquid nitroglycerine explodes with a moderate velocity of the order 1000–2000 m/sec, if the initiation of explosion is insufficiently strong.

A small diameter of the tube to be filled with the explosive favours a low rate of explosion. If this is very small, (a few millimetres) the velocity of propagation of explosive decomposition may be reduced to 700 m/sec, and is variable, so that the process cannot be regarded as detonation.

Nitroglycerine emulsified with a sufficiently large amount of water does not detonate. An emulsion of nitroglycerine can, however, detonate if it is composed of 150 parts (or less) of water and 100 parts of nitroglycerine, as reported by Médard [96]. The detonation rates of emulsions, when initiated with a No. 8 detonator are as follows:

water to nitroglycerine ratio	rate of detonation
75:100	6400 m/sec
100:100	5530 m/sec
150:100	5250 m/sec

TABLE 16

THE EXPLOSION AND DETONATION RATES OF NITROGLYCERINE

Conditions of loading and initiation	Rate of explosion m/sec	Author
Liquid		
Explosion		
Lead tube, 30 mm dia.	1525	Abel [83]
Narrow lead or tin tube, 3–6 mm dia.	1100	Berthelot and Vieille [84]
Iron tube 30 mm dia.	2050	Mettegang [85]
	1525	Blochmann [86]
Glass tube 22 mm dia. initiated by No. 8 detonator	1165	Andreyev and Dzerzhkovich [87]
	ca. 700	Ratner and Khariton [88]
Detonation		
Glass tube 24 mm dia. initiated by No. 8 detonator	8000	Hackel [17]
	7800	Cook [93]
Iron tube 25–37.5 mm dia. initiated by 1.5 g mercury fulminate	8525	Comey and Holmes [89]
Gas pipe, initiated by 50 g tetryl	7430	Günther [90]
Glass tube 22 mm dia. initiated by 10–15 g crystalline nitroglycerine	9100	Andreyev and Dzerzhkovich [87]
Steel tube 22 mm dia. initiated by 75 g PETN	7760–8240	Friedrich [91]
Tube 35 mm dia. initiated by No. 8 detonator	6500	Naoúm and Berthmann [92]
Tube as above, initiated by 50 g of picric acid	8580	Naoúm and Berthmann [92]
Crystalline		
Glass tube 21 mm dia. initiated by No. 10 detonator	8100	Chemisch-technische Reichsanstalt [94]
Iron crucible, initiated by No. 8 detonator	*ca.* 8000	Stettbacher [95]
Glass tube 22 mm dia. initiated by No. 8 detonator stable form	9150	Andreyev and Dzerzhkovich [87]
labile form	did not detonate	Andreyev and Dzerzhkovich [87]
labile form, initiated by 20 g tetryl	9100	Andreyev and Dzerzhkovich [87]
Glass tube, 24 mm dia., stable form initiated by No. 8 detonator	8220	Hackel [17]
labile form initiated by No. 8 detonator	*ca.* 8190	Hackel [17]

An emulsion composed of 200 parts of water and 100 parts of nitroglycerine is incapable of being initiated. In order to achieve complete safety, however, a ratio of 300 parts of water to 100 parts of nitroglycerine should be chosen.

In experiments designed to find the difference in the rates of explosion

between the labile and the stable forms of crystalline nitroglycerine Hackel found that both detonate with the same rate.

The occurrence of various explosion rates for liquid nitroglycerine has been explained by Audibert [97] by postulating two successive reaction stages. First a slightly exothermic chemical reaction (4a) would occur:

$$C_3H_5(ONO_2)_3 \longrightarrow 2\,CO + CO_2 + 2\tfrac{1}{2}H_2 + 1\tfrac{1}{2}N_2O + 1\tfrac{3}{4}O_2 + 21 \text{ kcal} \qquad (4a)$$

The decomposition of nitroglycerine can stop at this reaction stage if an initiation is weak and if the nitroglycerine is not confined. In these circumstances large quantities of N_2O are developed as the nitroglycerine decomposes. If initiation is strong enough and the nitroglycerine is confined, (e.g. in a tube) then a second reaction stage (4b) of distinctively exothermic character can follow:

$$C_3H_5(ONO_2)_3 \longrightarrow 3\,CO_2 + 2\tfrac{1}{2}H_2O + 1\tfrac{1}{2}N_2 + \tfrac{1}{4}O_2 + 319 \text{ kcal} \qquad (4b)$$

Audibert's theory seems to be correct only in certain cases. After a very vigorous initiation the final reaction probably takes place immediately and the maximum heat energy is developed.

Sensitiveness to flame. Attention has been paid recently (Andreyev [98]) to the fact that there is little precise information available concerning the sensitiveness of nitroglycerine to flame and its ability to burn. Naoúm states in his book [22] that nitroglycerine is difficult to ignite, yet burns readily. Unquestionably nitroglycerine burns without difficulty in the open air. However, it behaves otherwise when confined.

It was demonstrated by Andreyev that nitroglycerine placed in a glass tube of 5.18 or 22 mm dia. can be ignited with a gas flame or with a glowing wire. Burning is limited, however, to local decomposition and is not transferred to further layers. This phenomenon occurs both at room temperature and at 80°C. None the less an explosion can be brought about without preliminary burning if ignition of nitroglycerine is repeated on the same spot.

In Andreyev's experiments nitroglycerine burned in a vessel where the pressure had been reduced below the atmospheric pressure. The flame died out, however, when the pressure was increased beyond a certain limit, owing to the evolution of gaseous decomposition products. In the neighbourhood of that pressure, burning was very irregular. The critical pressure, when the flame of nitroglycerine is about to expire, depends upon the conditions of experiment, and varies between 234 and 375 mm Hg. The linear burning rate was estimated as 0.075 cm/sec.

At a temperature of 98°C the critical pressure was similar, while burning the rate increased significantly, to about 0.13 cm/sec.

Generalizing, Andreyev reported that nitroglycerine burns steadily at pressures below 400 mm Hg; the rate of burning depends on the pressure (Fig. 14) according to the equation:

$$U = 0.0067 + 0.216p^{0.831}$$

Among the products of burning, substances characteristic of incomplete decomposition of nitroglycerine, such as formaldehyde, can be detected. Extrapolating the curve in Fig. 14, Andreyev has determined the rate of burning for nitroglycerine at atmospheric pressure to be of about 0.23 g/cm/sec. Crystallized (frozen) nitroglycerine behaves the same as the liquid. Nitroglycerine with nitrocellulose dissolved in it (as for instance blasting gelatine) burns distinctly more readily than pure nitroglycerine and will burn under atmospheric pressure. Andreyev made the

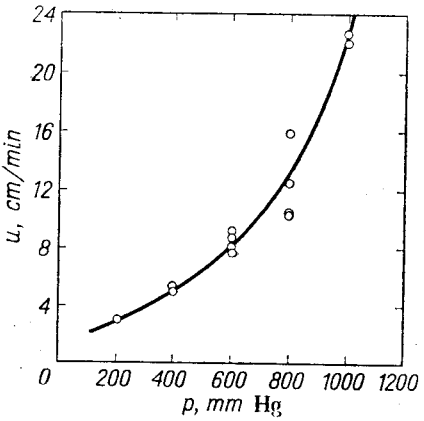


FIG. 14. Rate of burning of nitroglycerine as a function of pressure (Andreyev [60, 61]).

interesting observation that the higher the viscosity of the solution, the higher is the pressure at which marked increase of the burning rate occurs. A more detailed discussion of this is included in Vol. III.

Nitroglycol burns more readily than nitroglycerine, whereas dinitrodiglycol burns distinctly less so.

TOXICITY

References to the extremely powerful physiological activity of nitroglycerine were made as early as 1848 by Sobrero [1].

Nitroglycerine is a highly toxic substance. Its effect consists in dilating the blood vessels and thereby lowering the blood pressure.

Poisoning can take place either from inhalation of the vapour of nitroglycerine (the very low concentration corresponding with the vapour pressure at room temperature is sufficient) or as the result of penetration through the skin or through the mucous membranes (the latter occurs with particular ease).

The degree of sensitivity to the action of nitroglycerine varies to a large extent among different people. The chief symptom of nitroglycerine poisoning is a very severe headache which gives the impression that the head is being squeezed. Consumption of alcoholic drinks increases the toxic effect. The human body quickly becomes accustomed to the presence of nitroglycerine; often this accommodation

is complete after a few days work with it. However, the immunity is lost when the contact with nitroglycerine ceases and the worker's system must re-adapt itself when contact is resumed. Workers accustomed to close contact with nitroglycerine manage to knead dynamite dough with bare hands and to pass in through a sieve, without suffering any harmful consequences. Review of the medical literature (Schuchard [99], Evans [100], Ebright [101], Hudson [102]) indicates from many years of work that nitroglycerine produces no symptoms of chronic poisoning and that the substance should not be regarded as an industrial poison. It is exceptionally rare that individuals are found who cannot grow accustomed to handling nitroglycerine. Obviously any worker who fails to develop immunity should be transferred to other work. In cases of accidental poisoning (reported in the medical press) pain, vomiting, cyanosis, disturbances of the sight, swelling of extremities and paralysis have been observed. Rare cases of fatal poisoning have been reported. Antidotes include caffeine and analgesics (pain-relieving remedies) but the first step is to expose the patient to fresh air. In the case of slight poisoning the symptoms can be relieved simply by the latter treatment. Nitroglycerine headaches can be relieved by intramuscular injection of caffeine, sodium benzoate and oral administration of amphetamine sulphate (Rabinovitch [103]; Schwartz [104]).

After each shift, workers in the nitroglycerine department should change their clothing and have a bath, since accidents have been reported in which a worker returning home in his working clothes has caused his family to suffer from nitroglycerine poisoning (Lazarev [105]).

According to Weinberg [106] in the human system nitroglycerine is reduced to nitrous esters.

For many years the physiological effect of nitroglycerine in promptly decreasing the blood pressure has been used medically. It was used for the first time in about 1850 under the name glonoinum. For this purposes nitroglycerine is prepared in the form of a 1% alcoholic solution, which is given orally in doses of one or a few drops. The maximum single dose is 0.1 mg [107]. The present trend is to use other esters of nitric acid, namely erithritol tetranitrate (see p. 167), pentaerithritol tetranitrate (see p. 183), mannitol hexanitrate (see p. 171) and other similar derivatives instead of nitroglycerine to reduce the blood pressure. Being crystalline these substances are not so readily assimilated and therefore act more slowly and produce a longer lasting effect.

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CHAPTER III

PRODUCTION OF NITROGLYCERINE

TECHNOLOGICAL PRINCIPLES OF NITROGLYCERINE MANUFACTURE

THE O-nitration of glycerine and similar alcohols is a chemical reaction which is applicable on a large scale only by special technical methods. The technological processes used for manufacturing nitroglycerine and other similar nitric esters differ considerably from the current methods usually applied in the commercial production of organic compounds. These differences primarily concern the plant and are due to a large extent to the danger of the nitration process itself and also to the risks involved in handling both the product and the spent acids. In the manufacture of other organic chemicals the danger factor either does not exist or exists in a considerably smaller degree.

From experience gained over many years, special equipment and methods of nitration and purification of nitroglycerine have been developed and certain traditions established. Recently, however, changes have occurred in this field. Continuous methods of nitroglycerine manufacture have been introduced. In many cases they have revolutionized traditional techniques and led to new manufacturing processes.

Before describing individual production processes certain general principles will be outlined.

MIXED ACID COMPOSITION AND YIELD OF THE PROCESS

Theoretical calculation based on the equation of nitration shows that when 100 parts of glycerine are added to 205.4 parts of HNO_3 the yield is 246.7 parts of nitroglycerine. At the same time 58.7 parts of water are formed. In practice this yield cannot be obtained because the nitration of glycerine, like every esterification reaction, is in principle a reversible one. The yield is partly defined by the number of O-nitro groups introduced into the molecule of glycerol.

The stronger the acid concentration, the higher the degree of nitration and the larger is the yield. An excess of acids establishes equilibria that favour a more complete reaction. The surplus must not be too large, however, since nitroglycerine is slightly soluble in spent acid and this may considerably decrease the yield of

final product. For this reason it is necessary to formulate the nitrating acid so as to achieve as complete a nitration as possible while at the same time minimizing the loss of product due to its solubility in the spent acid.

Nitroglycerine can be obtained if nitric acid alone is used as a nitrating agent. In this case a large excess of acid should be used. One part by weight of glycerine mixed with 10 parts by weight of the strongest nitric acid (99%) below room temperature and afterwards diluted with 30 parts weight of water and ice yields 1.765 parts of nitroglycerine. From the separated spent acid a further quantity (0.307 parts by weight) of the substance can be extracted by means of chloroform. The total yield therefore amounts to 2.072 parts of nitroglycerine, containing a small admixture of "dinitroglycerine" (glycerol dinitrate), i.e. about 84% of theoretical yield.

If a smaller quantity of nitric acid is used in the process, e.g. 5 parts of acid with 1 part of glycerine, the yield decreases and the product represents a mixture of nitroglycerine and dinitroglycerine in the ratio of 1:3. Clearly an uneconomic procedure of this kind cannot have any practical application. Therefore even in the earliest experiments on nitroglycerine manufacture (Sobrero, Nobel, Zinin) a mixture of nitric acid and sulphuric acid was used for nitrating the glycerine. It was proved that for 1 part of glycerine a strong mixed acid containing 3 parts of nitric acid 90% and 4.5 parts of concentrated sulphuric acid could be used instead of 10 parts of anhydrous nitric acid, the yield being significantly higher, namely from 100 parts glycerine 215 parts of nitroglycerine, corresponding to 87% of the theoretical yield. The quantity of water should be below this required for $H_2SO_4 \cdot H_2O$ [53, 54].

Experiments on the use of mixtures of nitric acid with phosphoric anhydride showed this to be impracticable, since separate layers were formed with the phosphoric acid at the bottom and nitroglycerine remaining dissolved in the nitric acid layer from which it had to be separated by adding water. Nor was replacement of sulphuric acid by anhydrous calcium nitrate of any practical value, as precipitation of nitroglycerine by the addition of water was necessary. The yield attained by application of both these methods does not exceed 2 parts of nitroglycerine from 1 part of glycerol. At the time when concentrated nitric acid was very expensive, attempts were made to nitrate glycerine with a mixture of sulphuric acid and sodium nitrate (Huntley and Kessel [1]). However, this method found no practical use.

Considerable progress in the field of nitrating glycerine was achieved by Nathan, Thomson and Rintoul [2] who introduced oleum as a component of the nitrating acid, thus formulating an anhydrous mixed acid for the nitration process. Its application gave larger yields than nitration with acids containing about 5% of water. For example 100 parts of glycerine react with a mixed acid prepared from 280 parts of nitric acid 90% and 360 parts of oleum 20% to yield 225 parts nitroglycerine which corresponds with 91% of the theoretical yield. The development of improved equipment in full scale plant makes it possible to obtain 234 parts of nitroglycerine from 100 parts of glycerine, i. e. 95% of theory.

At present the most commonly used nitrating agent is the anhydrous mixed acid containing:

45–50% HNO_3
50–55% H_2SO_4

Mixed acid for nitration should be prepared from pure acids. The waste acids remaining after nitrating glycerine are not re-used in the nitration. They are subjected to a denitration process (more details are given on p. 84). In some factories nitrating acid is produced by mixing nitric acid with the spent acid which remains after the trinitration of toluene, afterwards concentrating the mixture by the addition of oleum. However such acid includes certain impurities, e.g. tetranitromethane, traces of which in nitroglycerine may exert a negative influence on the result of the starch–iodide paper test (heat test [3]). Where this procedure is adopted, during the final washing of nitroglycerine with sodium carbonate solution a small quantity of sodium sulphite should be added, since this combines with tetranitromethane to form a soluble sodium salt of trinitromethanesulphonic acid which can be removed with ease (see Vol. I, p. 589). In general, however, the use of spent acids in the preparation of mixed acid for the manufacture of nitroglycerine should be considered as improper. Indeed the use of spent acids for this purpose is forbidden, for instance, in the U.S.S.R. because despite special stabilizing methods (described above) nitroglycerine of satisfactory stability cannot be obtained.

Further, attention should be paid to the composition of the nitrating acid, for it is not without influence upon the stability of nitroglycerine and similar esters.

It has been demonstrated experimentally (L. P. Kuhn, W. J. Taylor and Groggins [4]) that increasing the D.V.S. (Vol. I, p. 139) favours high stability of the nitrator charge, while decreasing it results in reduced stability. This is explained by the fact that increasing the D.V.S. tends to shift the nitration or esterification further towards completion, whereas too low a D.V.S. would permit accumulation of incompletely nitrated material, along with increased dilution, and this would be favourable to oxidation reactions. It is also of interest to follow the changes in the value of the D.V.S. ratio during the course of nitration when glycerine is fed into the mixed acid. Since the amount of sulphuric acid is constant throughout the nitration and there is no water at the beginning of the nitration, the D.V.S. ratio is infinity until enough water has been formed to balance the initial negative water content. In a typical glycerine nitration this takes place after about 18% of the nitration has been completed. The D.V.S. ratio falls rapidly at first and then more slowly approaches the specified value which is reached at the end of the nitration.

One of the important factors in maintaining safety during nitration is the necessity for keeping the correct acid to glycerine ratio. In general too large a charge of glycerine in relation to the amount of acid present may lead to decomposition with a temperature rise accompanied by oxidation that is very often difficult to control.

The ratio mixed acid/glycerine should be such as to maintain an excess (*ca.* 20%) over the theoretical quantity of required nitric acid. The weight ratio mixed acid/glycerine is usually 5.5–6.5.

EQUIPMENT FOR PRODUCTION OF NITROGLYCERINE

For production of nitroglycerine a variety of equipment can be applied, depending on the method of manufacture to be used, that is either batch or continuous. In Europe the batch process of nitrating glycerine is performed in nitrators holding 150–250 kg glycerine, in South Africa 400 kg glycerine and in the U.S.A. 600 kg glycerine. According to MacNab [5] batch nitration was carried out with up to 1400 lb (635 kg) of glycerine. Continuous processes are much more efficient and safer in principle. Formerly the most commonly used construction material for nitrators (Fig. 15) was lead. This substance, used as long ago as the 1870's by Nobel, has many advantages.

(1) In the event of an explosion lead does not break into dangerous small frag-

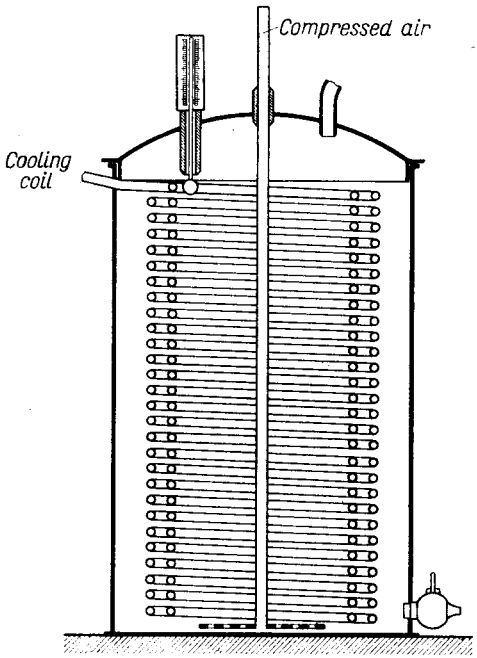

FIG. 15. Diagram of Nobel nitrator made of lead (Nobel, U.S. Pat. 57175 (1866), after Nauckhoff and Bergström [7]).

ments, but being a soft metal it is readily disintegrated or remains at the site of the explosion or in its neighbourhood as a lumpy mass. Iron vessels, on the other hand, break up if an explosion occurs and their destructive range may be considerable.

(2) Lead is an acid-resistant material and the lead sulphate formed on the surface does not contaminate the product of nitration, merely forming a permanent protective layer against the corrosive effects of the nitrating acids. However, the cover of lead sulphate acts as a thermal insulator, which is undersirable since it lowers efficiency of operation, e.g. when leaden cooling coils are used.

(3) Due to its softness lead can be struck or rubbed with less danger than that caused by striking or rubbing other materials, e.g. iron.

(4) Since it is a soft material, melting at a low temperature, lead is easily welded. In nitroglycerine plants, parts of equipment of lead can be constructed without difficulty in the factory's own workshops from sheet lead 10–15 mm thick.

Cast iron nitrators (Fig. 16) were used [6] more often than lead ones for nitrating nitroglycerine in the U.S.A.

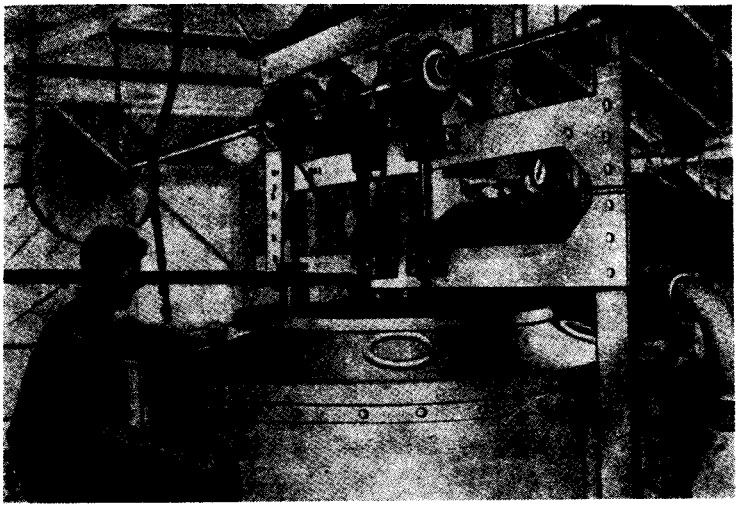

FIG. 16. U. S. nitroglycerine nitrator with two mechanical stirrers (*ca.* 1½ ton of nitroglycerine produced in one batch; Symmes [6]).

In the recently introduced continuous methods of nitroglycerine manufacture nitrators made from acid resistant steel are used since the art of welding stainless steel had progressed remarkably by the 1930's. The design and construction of nitrators for nitrating glycerine are included in the descriptions of individual methods of nitration.

Stirring

Good stirring of the mixture in the nitrator is a major safety factor and also important in securing a good yield. Lead nitrators have been equipped since Nobel's times with compressed air stirring, the pressure applied being usually 4 atm. Air nozzles are situated in the bottom of the nitrator in such way that no dead spaces remain. The efficiency of stirring is checked by putting corks on the surface of water led into the nitrator for test purposes.

If compressed air stirring is used, attention should be paid to the purity of air. Usually the air coming from the compressor contains a certain amount of lubricating oil. If this oil were to enter the nitrator it would react with the mixed acid and produce a dangerous rise in temperature. Thus the air must be purified before entering the nitrator. Generally a filter filled with coke or pumice is used.

Between the filter and the nitrator a reservoir of compressed air, fitted with a safety valve set for 4 atm pressure, should be installed. In the event of any breakdown in the compressor and any pause in the in-flow of compressed air, a steel cylinder filled with compressed nitrogen (or carbon dioxide) kept ready for this emergency should be used to supply gas to the stirrer pipe. While stirring is interrupted the supply of glycerine to the nitrator must be stopped.

Stirring by means of compressed air has a drawback, in that a certain quantity of nitric acid which is volatile is carried out of the nitrator and thus by decreasing the nitric acid content in the nitrator, can contribute to a diminished yield of the whole process. Experience has indeed shown that with mechanical stirring the output is usually higher by about 2% as compared with compressed air stirring.

The cast iron nitrators used in the U.S.A. are equipped with mechanical stirrers (Fig. 16).

According to Nauckhoff and Bergström [7] a nitrator with mechanical stirring was used as long ago as the 1870's: in 1872 in the British Dynamite Co. in Ardeer and in 1879 by A. Liedbeck at Isleton in Switzerland, Paulilles in France and Avigliana in Italy.

Nowadays nitrators for continuous nitration made from stainless steel are fitted with high-speed mechanical stirrers operating at up to 600 r.p.m.

The method by which glycerine addition is carried out also exerts an influence on the uniformity of the nitration process. There exist several arrangements by means of which the nitrator can be supplied with glycerine, in the form of a few up to about twenty thin streams or in a finely divided state. On the basis of long years' experience it has been found, however, that the method of adding the glycerine to the acid is a secondary factor in comparison with stirring. Hence glycerine can be added as a 1–1.5 cm stream without any trouble, if the contents of nitrator are well stirred.

Since the viscosity of glycerine is high, especially at low temperatures, it must be warmed before it is introduced into the nitrator. In practice glycerine is warmed to 25–40°C. At a lower temperature its viscosity is too high, and at a more elevated temperature there is a danger that the temperature could be too high at the moment of contacting glycerine with the nitrating mixture and that decomposition of the nitroglycerine formed thus could take place. Because of its low viscosity at temperatures between 25 and 40°C the stream of glycerine is easily dispersed in the nitrating acid by stirring.

There are special devices which make it possible to introduce glycerine to the nitrator by means of compressed air if a convenient inlet valve is opened manually by pressing with the hand. Then, if there is any danger of an explosion (e.g. if the temperature is too high, and brown fumes are formed), the glycerine supply must be stopped quickly. The workman in change of the nitration can do this easily for simply by lifting his hand he stops the stream of glycerine.

Immediately after the full charge of glycerine has been added and the stirrer stopped, the glycerine feed arrangement should be removed from the nitrator in

order to make sure that no more glycerine falls into the nitrator while there is no stirring. One drop of glycerine can bring about a dangerous explosive decomposition in these circumstances. An accidental explosion occurred in an emptied nitrator which was partially destroyed when a drop of glycerine fell to the bottom of the vessel onto remnants of spent acid and initiated remnants of nitroglycerine.

Equipment is also available for spraying glycerine under the surface of the nitrating acid. This arrangement does not offer any special advantages and is liable to be easily corroded in the presence of acids.

NITRATING TEMPERATURE

Experience has shown that within certain limits the lower the temperature of nitration, the higher the yield of nitroglycerine. This fact can easily be explained, because the higher the temperature of nitration, the more intensive the oxidation reactions. The nitration of glycerine may be performed on a small scale at a temperature of 40°C, but its yield is then rather low. In large scale manufacture, however, this temperature is to be considered dangerous, the more so since thermometers seldom show the temperature in the centres of decomposition, only the average temperature, so that locally the temperature can be markedly higher and sufficient to produce a spontaneous decomposition process which usually ends in an explosion. The maximum temperature allowed for nitration on plant scale is usually 30°C. On the other hand a very low nitrating temperature (e.g. about 0°C) is not recommended, as the nitration then proceeds too slowly.

A nitration temperature within the limits 30–35°C should not be considered dangerous and is often applied in some factories (e.g. Gyttorp [7]). However, should any irregularity occur which may be accompanied by an increase in temperature, obviously less time will be available to lower it than if the working temperature is lower (e.g. 20–25°C).

Stirring and cooling to keep an even temperature that does not rise above a certain limit, is an essential feature of the nitrator. During the nitration of glycerine a large amount of heat is produced; 120–170 kcal/kg glycerine are developed in the reaction of esterification plus about 200 kcal/kg glycerine due to dilution of the acid. The cooling arrangements must be able to remove, rapidly, the heat liberated. Until suitable equipment became available the nitration of large amounts of glycerine always presented a serious danger. Initially, efforts were made to modify the manufacturing process itself by dividing it into two stage (Boutmy and Faucher method [31] see p. 88). Afterwards Nobel [8] designed nitrators carrying leaden coils having a very large cooling surface and having an outer jacket. It was found, however, that the jacket is superfluous and that cooling by means of coils is entirely adequate, provided of course that the coils are fed with sufficiently cold water. Later the efficiency of the cooling arrangements was further increased by using brine or spirit at temperatures below 0°C. In effect nitrating temperatures of about 12°C can be maintained, increasing the yield by 3–4%.

The relation between the temperature of nitration and the yield of nitroglycerine is especially marked if less concentrated mixed acids are used. According to Naoúm's data, nitrating glycerine in mixed acid containing

39.0%	HNO_3
55.5%	H_2SO_4
5.5%	H_2O

at 30°C yielded 205% nitroglycerine, whilst nitration at 0°C increased the yield to 217%.

The yield differences are smaller if the acid contains less water. Thus, by using mixed acid comprising

38.7%	HNO_3
58.6%	H_2SO_4
2.7%	H_2O

in the ratio of 6.5 parts of acid to 1 part of glycerine at different nitrating temperatures the following yields were obtained:

at 30°C	216%
at 10°C	223%
at 0°C	225%

When nitration is carried out in an anhydrous mixed acid at a temperature of 30°C the yield is about 4–4.5% smaller then when nitrating at 0–10°C.

Temperatures below 12°C are not usually used, since crystallization of nitroglycerine could take place. Lower temperatures (e.g. 5–7°C) can be applied only when a mixture of glycerine with glycol or diglycerol is nitrated and if there exists no fear that the mixture of esters resulting from the reaction can freeze. In factory practice, nitration is performed mainly at temperatures of about 20–25°C or at 25–30°C. The temperature is measured by means of at least two thermometers, immersed in the vessel at different depths.

A temperature increase in the nitrator accompanied by the evolution of red-brown oxides of nitrogen indicates that dangerous decomposition and oxidation processes are occurring. Should these danger signals occur, the glycerine supply must be stopped instantly. Then, after waiting for a time, if the temperature does not fall but tends to remain high or to increase further, the contents of the nitrator should be let down into a special drowning tank.

At the beginning of each day's work the cooling coil should be checked to ensure that it is not damaged. A minute hole in the coil can bring about decomposition and explosion, due to the heat developed by the cooling water penetrating to the acid through the hole and causing the temperature to rise above the permitted limit. The condition of the coil can be checked in different ways. The best method is to remove all water from the coil, to fill the nitrator with acid and to attach the compressed air line (of 3–4 atm) to the coil. Bubbles of air appearing on the surface of acid indicate that the coil is not leakproof. Another method of checking that the equipment is undamaged consists in the following operations: an evacuated

nitrator is allowed to stand over night, with the water inlet valve of the coil open, the outlet valve being shut. If there are any holes in the coil, water will be found in the nitrator after a few hours.

Damage to the leaden coil also may be brought about by excessively high water pressure. In order to avoid this, low pressures of water or an alternative cooling medium should be used. The weaker parts of the coil may be expanded by the action of water and the weakened place then attacked by corrosion. Welds are also liable to undergo corrosion and welding should therefore be carried out with great care.

In some factories a suction system is used for the water or cooling liquid in place of a pressure system. In such systems, slight damage of the coil may be less dangerous, because the cooling liquid does not escape from the coil into the nitrator or only to a very small extent, so that it is possible to complete the nitration without undue risk.

In addition to carrying out all the checks which have been discussed and adopting appropiate safety measures, an extra routine precaution to be recommended consists in changing the old leaden coil for a new one after a certain number of nitrations have been carried out.

DROWNING TANK

If decomposition begins in the nitrator with increasing temperature and evolution of brown fumes, it is necessary to make the contents of the nitrator harmless by discharging the whole into the drowning tank.

Decomposition can be caused by the following factors:

(1) insufficient purity of the glycerine, especially if sugars and fatty acids are present;

(2) defective stirring and insufficient purity of the compressed air;

(3) unadequate cooling or leaks in the cooling coil.

The nitrator should be fitted with a safety outlet of such a cross-section that the nitrator contents can be discharged into the drowning tank in a period not longer than half a minute.

The drowning tank is situated beneath the nitrator. It is constructed of concrete or of wood lined with lead or stainless steel.

Its capacity should be about 10 times greater than that of the nitrator, and it should be half filled with water. An inlet pipe feeds compressed air into the bottom of the tank and the air supply should be turned on simultaneously as the safety valve is opened to evacuate the nitrator. Another solution consists in simultaneously opening the nitrator and injecting a strong jet of cold water before the mass enters the drowning tank.

Alternatively, drowning tank may be filled with concentrated sulphuric acid. In this case, nitroglycerine is not precipitated, but remains in solution. On mixing with sulphuric acid less heat is evolved than is developed on stirring with water. As result of both these factors, decomposition ceases, whereas after passing into water, decomposition continues although the charge has been diluted.

The evacuation of nitrator should proceed with the greatest possible speed and immediately after the respective valves are opened the personnel should leave the nitration room. Good discipline and the ability to think and act quickly are essential in the employees (more especially in the nitration foreman). In order to facilitate operations at times of crisis, various automatic devices are used to ease the manipulation of the valves. When a single lever is touched or a single button pressed these devices simultaneously actuate, for example,

(1) the discharge valve emptying the nitrator into the drowning tank,

(2) the compressed air valve feeding the drowning tank and

(3) the inlet valve supplying compressed air to the danger warning whistle.

One of the simplest arrangement of this type is illustrated in Fig. 17. By means of the lever (*1*) the inflow of compressed air into the cylinder (*2*), furnished with

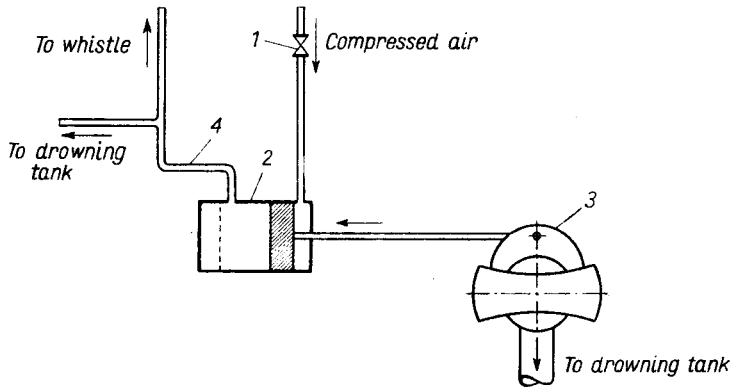

FIG. 17. Automatic quick discharge of the nitrator to the emergency drowning tank.

a movable piston, is started. The movement of the piston in the direction indicated by the arrow opens the valve (*3*) which empties the contents of nitrator. When the piston is pushed through to its farthest position the compressed air passes out, via the pipe (*4*) to the drowning tank and to the whistle. The efficiency of any automatic safety device should be checked before every nitration.

NITRATION TIME

The nitration rate depends, of course, on the concentration of the nitrating acid, on stirring and on the temperature. At the beginning, in the fresh anhydrous mixed acid, glycerine is nitrated at a high rate. According to Oehman [53] 80% of glycerine is nitrated within less then 1 sec. The reaction occurs mainly on the interface between the two reacting phases. As the nitric acid is consumed and water is produced the reaction rate gradually decreases. When the nitration is nearing completion (after 2–6 sec) the mixture of acids contains in addition to nitroglycerine (which is present mainly in suspension and only to a small extent in solution) dissolved glycerol dinitrates, the so called dinitroglycerines (*ca.* 4.5% according

to Oehman [54]), as well as mixed esters of nitric and sulphuric acid. These substances react gradually with the nitric acid in the mixed acid to give further quantities of nitroglycerine [27]. However, this process, which is called the secondary separation of nitroglycerine, requires a long time and it cannot be included in the nitration period proper as this should be accomplished in the shortest possible time (for details concerning this process see p. 95). There exist methods (Nathan, Thomson and Rintoul, Biazzi) in which, for various reasons, the possibility of utilizing these esters is ignored, and the secondary separation process omitted (see pp. 84, 91, 107).

Above all the time of batch nitrating depends on the cooling surface, on the temperature of the cooling liquid and on the intensity of stirring. It is also related to the size of the glycerine charge. On the average the nitration of 100 kg of nitroglycerine is completed in 20 min, if the temperature of the cooling water is 10–12°C and the temperature in the nitrator is 30°C.

The original temperature of the mixture of acids also exerts its influence on the period of nitrating; the lower it is the sooner the glycerine can be introduced into the nitrator. In winter, nitration takes less time due to this factor.

In nitrators equipped with mechanical stirrers, as used in the U.S.A., 500 kg of glycerine are nitrated in 50 min.

SEPARATION OF NITROGLYCERINE FROM ACID

Originally nitroglycerine was separated from the spent acid by pouring the whole contents of the nitrator into a wooden tank containing a large amount of water. Afterwards the aqueous solution from above the nitroglycerine was decanted. This operation was troublesome and dangerous since on dilution a large quantity of heat was evolved. Further, this method was uneconomic for it was impossible to recover the spent acid. Later, the technique of removing the nitroglycerine with a ladle from above the waste acid was introduced, and finally modern methods have been applied to the separation process.

For several minutes after the nitrator has been fully charged, stirring is discontinued and then either the whole is allowed to remain in the nitrator which in this stage plays the part of separator, or it is transferred to a special separating funnel. In continuous production the mixture flows into the separator continuously.

All methods of separating nitroglycerine from acid take advantage of the difference between the specific gravities of the two liquids. Experience has shown that the purity of glycerine to be nitrated and the purity of the nitrating acid exert a big influence on the rate of separation of the two layers. It has been proved that fatty acids, which frequently occur as impurities in glycerine, delay separation. Similarly the separation rate of the two phases is decreased by the fine crystalline precipitate of sulphate (of lead or iron) which is present in the spent acid as a suspension. All colloidal components in the glycerine and in the acid also slow down the phase separation.

Normal separation of phases should be complete in 20–30 min. However, under

unfavourable conditions the time required may extend to several hours or more, and in this event separation can become a dangerous operation. Several serious explosions took place (between 1904 and 1912) during the separation of nitroglycerine from spent acid. In most of these incidents the explosion was caused by the lengthy period of contact between nitroglycerine and spent acid, resulting from the too slow separation of the nitroglycerine layer.

Much experimental work designed to accelerate the separation of nitroglycerine from spent acid has been carried out. It has been established that the separation can be hastened in several ways:

(1) Using shallow separators having a large surface area in which the distance to be travelled by drops of nitroglycerine is as short as possible.

(2) Raising the temperature to 18–20°C in the final stage of nitration. This is recommended if the nitration has been carried out at a low temperature, e.g. 12–15°C, since separation of the layers proceeds too slowly at such temperatures.

(3) Adding certain substances to the emulsion of nitroglycerine in acid, which have been shown to accelerate phase separation. The first experiment in which a marked increase in the rate of separation of the phases was achieved was reported in 1904 by Naoúm [9] who added non-polar substances which do not undergo nitration, e.g. paraffin oil, vaseline, in the proportion 0.05–0.2% of glycerine by weight, towards the end of nitration. The paraffin oil remains in the nitroglycerine layer, to be removed afterwards when the nitroglycerine is washed with water. By this means the time of separation was halved in the factory at Krümmel. To the charge of 250 kg glycerine and 1600 kg mixed acid 100 ml of paraffin oil were added, thereby reducing the separation time from 30–40 min to 15–20 min.

In the Dynamite Works at Wilmington, the addition of sodium fluoride to hasten separation has been suggested by Reese [10]. Sodium fluoride has been chosen on the assumption that rapid separation is hindered due to silicic acid and silicates present in the nitrating acid. These impurities would be removed by reaction with hydrofluoric acid to form silicon fluoride. It is true that in the presence of sodium, fluoride separation is easier, though the reasons for its effect are different than those indicated by the inventor. In fact, it has been demonstrated by the investigations of Rheinische Dynamitfabrik, Opladen, 1912 [11] that with chemically pure sodium fluoride the separation of the phases is not accelerated. The commercial product however, containing silica and silicates, has a positive effect. Thus silicon fluoride, SiF_4, seems to be the factor which accelerates the separation of phases, as it is produced in the form of bubbles which flow towards the surface of the liquid simultaneously carrying up the nitroglycerine. For this reason the patent [12] based on these experiments recommends adding either a mixture of sodium fluoride with silica or with fluorosilicate. In either case silicon fluoride is formed according to the following reactions:

$$4NaF + SiO_2 + 2H_2SO_4 \longrightarrow 2Na_2SO_4 + H_2O + SiF_4 \quad (1)$$

$$Na_6SiF_6 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HF + SiF_4 \quad (2)$$

In the second case it is possible to take advantage of the resulting hydrofluoric acid by addition of silica to produce further quantities of silicon fluoride. As reported in the patent, to a 150–200 kg charge of glycerine approaching the end of nitration, about 30 g of a mixture composed of sodium fluoride and silica are added. If the addition is made too soon its effect is lost, since the SiF_4 is carried away by the air stream and removed from the system.

Other proposals have also been published, e.g. the suggestion of Westphälisch-Anhaltische factory [13] to add 0.02–0.05% of talc. Another way of hastening the separation is found in a patent of Carbonit A.G. in Hamburg [14], wherein additions of about 1% urea, acetamide or dicyandiamide (calculated in relation to glycerine) to the mixed acid are recommended. In contact with acid these substances decompose to form gaseous products which hasten separation in the same way as silicon fluoride.

The quantitative effect of various additives on the rate of separation of nitroglycerine from spent acid has been determined by Moisak and Grigoryev [15]. They found that in the presence of 0.5% ferric sulphate or lead sulphate, the separation rate is halved. Further, they established that the separation rate is related to the composition of the spent acid. The maximum rate of separating was achieved by using acid composed as follows:

HNO_3	17%
H_2SO_4	70%
H_2O	13%

An interesting attempt was made by Lehmann [16] to use an electrochemical method to speed up the separation of nitroglycerine. His theory was that gas evolved in the course of electrolysis would help nitroglycerine to rise to the surface.

PURIFICATION OF NITROGLYCERINE

After being separated from the spent acid, nitroglycerine still contains about 10% of acid. The composition of the acid absorbed by the nitroglycerine is different from that of the acid forming the lower layer in the separating funnel, because nitric acid is absorbed by nitroglycerine more than sulphuric acid. The H_2SO_4 to HNO_3 weight ratio in the spent acid has a value of 9, whereas in the acid absorbed by nitroglycerine the ratio is approximately 1:4 (this was discussed earlier, on p. 42).

The greater part of the acid absorbed in the nitroglycerine is removed in the primary washing, which is carried out with cold water of about 15°C, usually in the same room as the nitrator. This primary washing is insufficient to remove the last traces of absorbed acid which are very difficult to eliminate. The product is therefore washed again first with hot water, then with a dilute solution of sodium carbonate (2–4%), again with hot water and finally by a cold water wash. The temperature of the hot water and sodium carbonate solution should be held at such a level, e.g. 60–70°C, that the whole contents of the washing tank can be kept at a temperature of e.g. 45–50°C. The last cold wash, referred to as stabilization, is carried out in a separate room, into which acid vapour from the nitration room should not be allowed to penetrate.

The washing of nitroglycerine would seem to be a simple and safe operation. Nevertheless numerous explosions have occurred even in the washing tanks. Explosions of this kind were the more unexpected as right from the start compressed air was used to mix the nitroglycerine with the water or carbonate solution, so that there was no risk of friction between metal parts. In 1903 in Great Britain 9 incidents of explosion in washing tanks were recorded. Analysis of the accidents indicated that a few of them may have occurred due to friction of nitroglycerine in the numerous stop-cocks situated beside the tank controlling the outflow of liquid. Several other explosions were probably caused by the fact that the compressed air supply line serving the bottom of tank was lying loose on the bottom. The introduction of air could cause the pipe to move and to strike the walls of tank exploding the nitroglycerine. For these reasons in the construction of washing tanks (washers) outlet cocks for the liquid are omitted, and the compressed air delivery pipe is rigid and attached firmly to the bottom of tank.

The design of the most widely used type of nitroglycerine washing tank is illustrated in Fig. 18. The tank of a cylindrical shape is constructed of sheet lead

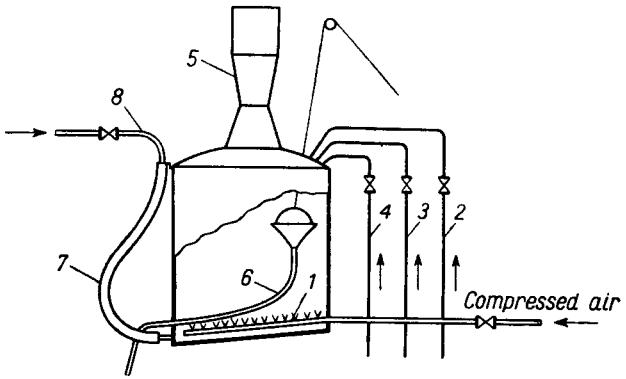

FIG. 18. Design of the tank for washing nitroglycerine (Naoúm [11]).

or of a resinous wood (e.g. pitch-pine) since lead can readily undergo corrosion. It is equipped with the device (*1*) for delivering compressed air, pipelines (*2*) for cold water supply, and pipes (*3*) and (*4*) for hot water and sodium carbonate solution respectively. It is desirable to equip the tank with a conical lid with a ventilation duct (*5*), for carrying off acid vapours evolved during the preliminary washing of the nitroglycerine, and vapours of nitroglycerine given off during hot washing. The hose pipe (*6*) ending in a funnel is used for lowering the upper layer of liquid. An accident occurred in 1894 [17] in which the rope holding the funnel was broken off and the heavy leaden funnel weighing over 10 kg fell into the warm nitroglycerine (*ca.* 50°C) and caused it to explode. Since then the funnels are made of thin tin plate, sheet copper or sheet brass. The funnel is fastened to a cable drawn over a pulley fixed in the ceiling.

The lower layer, i.e. nitroglycerine, is discharged from the tank through the rubber hose (*7*) which is normally kept raised in a higher position by means of a hook

fixed on the upper edge of the tank, so as to close the outlet. In order to open the nitroglycerine outflow the hose (*7*) is lowered. After washing the nitroglycerine, compressed air is applied to the hose (*7*) by means of pipe (*8*) to expel the nitroglycerine collected in the lowest part of the hose and to transfer it to the stabilization process. The tank should be equipped with a thermometer (which is not shown in the illustration) to check the temperature of the nitroglycerine. The diameter of the tank should be as large as possible and not less than its height. With these dimensions the precipitation of nitroglycerine in water proceeds rapidly and may take some 10–15 sec. It has been demonstrated experimentally that in a liquid column of 70 cm separation is accomplished after about 30 sec, while at a depth of 47 cm it requires only about 10 sec.

If hardwash-water is used, sedimentation of calcium carbonate occurs in the air supply lines. This materially increases the danger of handling the nitroglycerine since calcium carbonate is hard and its surface is uneven and friction between nitroglycerine and a surface of this kind is more dangerous than contact with the smooth surface of pure lead. For this reason hard water intended for washing should be softened before use. Water of high purity should always be used. In accordance with a report by M. Jacqué [18] at one of the dynamite plants in Mexico great difficulty was experienced in obtaining nitroglycerine capable of passing a 15-min heat test at 76°C. Systematic experiments showed that the poor stability of the nitroglycerine was caused by organic pollution of the wash water, derived from sea-weed and plankton. The difficulty was over-come by careful purification of the water supply.

In different factories various methods of nitroglycerine purification are used. A description of the British method was given by Marshall [19]. The primary washing with water at the temperature of 18°C is repeated three times to be followed by the last, fourth, washing with sodium carbonate solution. Afterwards nitroglycerine is discharged through a pipe to undergo the final washing at 30°C (the temperature inside the tank). The final washing comprises five stages;

(1) 15 min with a solution of 3.5% Na_2CO_3
(2) 30 min with a solution of 3.5% Na_2CO_3
(3) 45 min with a solution of 3.5% Na_2CO_3
(4) 15 min with softened water 3.5% Na_2CO_3
(5) 15 min with softened water 3.5% Na_2CO_3

The amount of water or solution to be used equals 2.5 parts by weight to 1 part of nitroglycerine.

Following the findings of Naoúm [11] the first washing with cold water at 15°C is succeeded by a series of washings with water wherein a larger and larger quantity of hot water is utilized. Nitroglycerine is rinsed in this way 3 or 4 times, to attain in the last washing a temperature of 40°C. Each washing lasts 5 min and consists in vigorous stirring of the nitroglycerine and water, after which the water is decanted.

Afterwards, washing with a 2–3% sodium carbonate solution heated to about 70°C takes place. After the solution is poured into the tank with the nitroglycerine

the temperature inside the tank reaches about 50°C. Similarly, each washing with carbonate solution consists in stirring up the contents of the tank for 15–20 min, after which the upper solution is decanted. The decanted solution ought to give an alkaline reaction to phenolphthalein. If not, washing with sodium carbonate solution should be repeated.

After being washed with carbonate, nitroglycerine is subjected to a final washing with water: at first with hot water at 50–70°C and finally with cold water, in order to remove the sodium carbonate completely. Frequently the washing operations are shortened to 5 min except for the sodium carbonate wash, which lasts each 15 min.

The washed nitroglycerine should be neutral to litmus. If the nitroglycerine is to be used in the manufacture of mining explosives for immediate use, in certain countries the litmus paper test is considered to be a sufficient criterion of purity. If, however, the nitroglycerine is destined for the production of smokeless powders or high explosives which are to be transported to distant places, the heat test should be used to determine the purity of the nitroglycerine. German regulations require that nitroglycerine for smokeless powder manufacture should withstand the zinc iodide–starch paper test for at least 20 min at a temperature of 82°C. Nitroglycerine to be used for the production of high explosives should withstand the test with the less sensitive potassium iodide–starch paper for at least 10 min at 72°C. If a sufficiently high purity nitroglycerine cannot be obtained by means of the normal washing with sodium carbonate solution a supplementary washing with sodium carbonate solution (2–3%) containing 0.1–0.2% sodium sulphite is recommended. The addition of sodium sulphite is especially efficacious when nitroglycerine is contaminated with tetranitromethane contained in nitrating mixture prepared from spent acid from trinitrotoluene manufacture (see also p. 64). In the modern Biazzi process (p. 107) nitroglycerine is washed with 12% sodium carbonate solution without preliminary treatment with water.

Recently stabilization of nitroglycerine and nitroglycol by passing them through a layer of substances adsorbing the residual acids remaining in the nitroglycerine washed by the usual methods has been suggested (Ropuszyński [20]). Nitroglycerine purified in the usual way contained 0.0056% HNO_3 and 0.0010% H_2SO_4 and withstood the heat test at 72°C for 27 min. After passing this nitroglycerine through a layer of aluminium oxide or an anion exchanger (the commercial product Wofatit MD was used) nitroglycerine containing practically no acids and withstanding the heat test for 50 min has been obtained.

The same author (Ropuszyński [21]) claims a slight improvement in the stability of nitroglycerine achieved if it is washed with water or aqueous sodium hydrogen carbonate in a magnetic field.

For instance nitroglycerine after preliminary washing (sample 1) was stabilized by washing with water (sample 2) or by washing in a magnetic field (sample 3) at 23.0°C. The pH of samples heated for $1\frac{1}{2}$ and $2\frac{1}{2}$ hr at 110°C were measured:

TABLE 17

Sample	pH after	
	1½ hr	2½ hr
	at 110°C	
1. Washed	2.78	2.75
2. Stabilized at 23°C	2.97	2.70
3. Stabilized in magnetic field at 23°C	3.13	2.92

FILTERING NITROGLYCERINE

After washing, nitroglycerine is turbid, because water in the form of emulsion and an insignificant quantity of mechanical impurities are dispersed in it. Both are usually eliminated by filtering through woollen material (flannel). The fabric may be loosely covered with a layer of crystalline common salt in order to facilitate the separation of water through the salting out phenomenon. It is also possible to separate water and nitroglycerine simply by settling. Water rises to the surface to form globules which can be removed with a ladle, and the turbidity is reduced.

If the filtered nitroglycerine is still turbid owing to the presence of water in suspension, it is usually allowed to stand quietly for a day and night or longer. Throughout this time the nitroglycerine grows clearer and its content of water decreases to 0.3–0.4%, whereas immediately after filtering the water present may amount to about 0.5%.

The filtrating installation comprises leaden tanks arranged on two or three levels (Figs. 19 and 20).

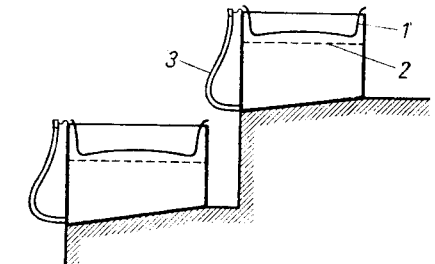

FIG. 19. Diagram of filtration of nitroglycerine through flannel: *1*—flannel, *2*—net, *3*—rubber hose.

The tank situated on the uppermost level is fed with recently washed nitroglycerine through a pipe or gutter. The lower tanks are covered with a fine brass mesh on which flannel is laid. The flow from the upper to the lower tanks proceeds via rubber

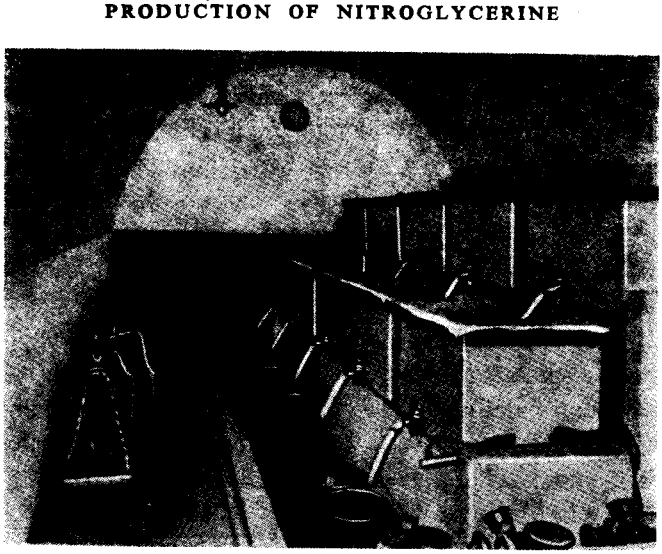

FIG. 20. General view of filtration room (Naoúm [11]).

hoses or by hooking the hose at the appropriate height. The flow is regulated mechanically by tightening a screw clip. In some factories ebonite stop cocks are used. The use of stoneware cocks is not considered to be safe enough.

An alternative is to filter the nitroglycerine through a thick layer of common salt (Fig. 21).

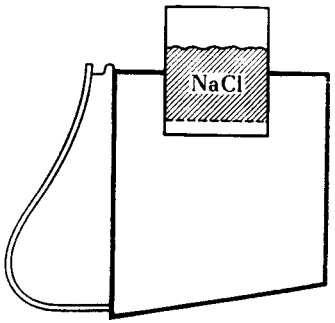

FIG. 21. Diagram of filtration of nitroglycerine through common salt.

Generally the filtration unit is situated in a separate building where the finished nitroglycerine is also stored. Here the nitroglycerine is weighed on a non-ferrous balance, before being transferred to further production.

TRANSPORT OF NITROGLYCERINE

Formerly after primary washing nitroglycerine was transported from the nitration unit to the stabilization room by means of a gutter-shaped leaden pipeline, furnished with a jacketed bottom heated in the winter with hot water. The tempera-

ture of the gutter was controlled by means of thermometers. In order to safeguard the nitroglycerine from mechanical contamination the gutter was covered with canvas or with wooden lids. Now aluminium pipelines are used, rubber hoses (sometimes made of conductive rubber to avoid production of static electricity) or even glass pipelines equipped with a jacket and heated with hot water during cold weather. To facilitate the flow of nitroglycerine the pipeline slopes downwards slightly. Explosion traps are inserted in the nitroglycerine pipe-line to prevent the spread of explosion should this occur. Various types are used:

(1) The pipeline (or gutter) includes several bends. Since liquid nitroglycerine has relatively little inclination to detonate it is highly likely that an explosion might be quenched at one of the curves.

(2) Part of the pipeline (or gutter) between buildings is replaced for a distance of about 1 m by narrow-bore hose of about 10 mm dia. Any explosion will be quenched at this point, because within pipes of this diameter nitroglycerine cannot readily detonate.

(3) The nitroglycerine conduit is equipped with a special detonation breaker. The detonation breaker (Fig. 22) is a lead tank filled with water to half or two thirds

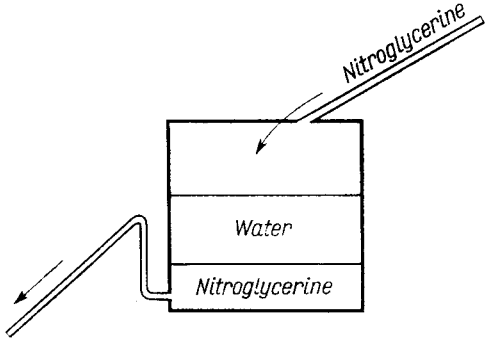

FIG. 22. Diagram of a detonation breaker.

capacity. Nitroglycerine flows into the tank, collects on the bottom and runs on from below through the siphon. This arrangement interrupts the nitroglycerine stream. Detonation cannot be transferred readily through the water barrier.

For a time professional publications recommended carrying nitroglycerine by hand from one site to another in ebonite or brass pails. However, in practice this method of transfer was responsible for many catastrophic accidents caused for instance when the workman carrying the nitroglycerine fell, stumbled or slipped.

The transport of stabilized nitroglycerine to the rooms where it is to undergo final purification, e.g. filtration through a flannel, is now performed by means of a pipeline. In order to increase the safety of this operation, an emulsion of nitroglycerine in water or in an aqueous solution of sodium carbonate is produced by means of an injector and this emulsion is run through the pipeline.

As a safety measure, the ratio of water to nitroglycerine should be not less than 3:1, since at 1.5:1 the emulsion can detonate as shown by the investigations of Médard [22] already quoted (see p. 54).

It is important to make a stable emulsion which does not tend to form separate layers. The addition of surface active agents is recommended. According to Desseigne [23] non-ionic emulsifying agents formed by the condensation of ethylene oxide with higher alcohols, e.g. cetyl or oleyl alcohol should be used. The addition of protective colloids such as Tylose DKL (carboxymethylcellulose) makes it possible to economize considerably in the quantity of surface active agents required. For instance 0.5% of an emulsifier and 0.2% of carboxymethylcellulose may be added to the water. Tranchant [24] is of the opinion that the emulsifier mentioned above does not affect adversely the stability of the nitroglycerine if its concentration is 0.5% or less.

The emulsion of nitroglycerine is allowed to run into separating tanks in which the components are separated into two layers by an upward flow of water. Nitroglycerine is discharged from the bottom of the tank and passes to the filters.

Finally the purified, stabilized and filtered nitroglycerine is transported from the store to the departments where it is required for further manufacturing processes (to make dynamite or smokeless powder). When required for smokeless powder manufacture, nitroglycerine can be transported as an aqueous emulsion by means

FIG. 23. Nitroglycerine truck (du Pont de Nemours Co. Repauno) (Marshall [19]).

of pipelines as described above. Where dry nitroglycerine is required for dynamite manufacture manual transport is used. From the safety point of view, this should be mechanized as far as possible. Thus the vessels containing nitroglycerine are carried in hand trucks equipped with good leaf springs and rubber-tyred wheels, which travel paths of wood, asphalt or concrete between the buildings (Fig. 23).

Nauckhoff [25] invented a special transport device for nitroglycerine which was

introduced in the nitroglycerine factory at Gyttorp (Nitroglycerin A. B. Gyttorp). It comprises a rail over 2 m high on which a container is suspended. The rail and suspended container (*1*) are shown in Fig. 24. The container is filled by sucking nitroglycerine from the transit tank (*2*). In the mixing compartment nitroglycerine is transferred from the container (*1*) to the kneading machine (*3*) by means of compressed air.

Transport of liquid nitroglycerine from the nitroglycerine factory to another plant is not allowed in Europe. It can be transported only in mixed forms: as dynamites or semi-finished mixtures ready to be used for the manufacture of mining explosives or of double base powders. Only in U.S.A. is the transport of nitroglycerine in special trucks allowed.

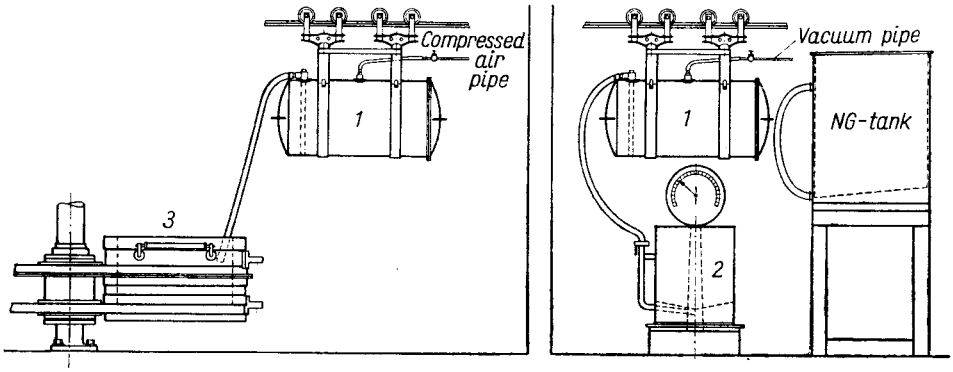

FIG. 24. Nitroglycerine transport device S. Nauckhoff system, Gyttorp 1919 (Nauckhoff and Bergström [7]).

RECOVERY OF STABILIZING WATER

Some 2% of nitroglycerine remains in the water and in the sodium carbonate solution used for washing. In the early days of the manufacture of nitroglycerine the whole of the waste wash water was allowed to flow into a river or pool, when the nitroglycerine slowly decomposed, under the influence of direct sunlight in the presence of water. Clearly, in these conditions decomposition was rather slow and in certain circumstances more and more nitroglycerine accumulated, and unfortunate accidents occurred. One explosion occurred on a river bank near to an outlet carrying waste wash water. Its cause was discussed by Naoúm [11]. In rowing a boat away, the oarsman struck the rocky bank with a metal-clad oar and initiated an explosion which killed him and destroyed the boat.

According to present practice polluted waste water flows into special trough-shaped tanks or labyrinths (Fig. 25), made of lead, stoneware or preferably of rubber-covered iron, and equipped with transverse baffle plates.

The waste water is thereby made to travel a long distance during which drops

of nitroglycerine settle out on the bottom of the labyrinth. Since acid water from the first washing is mixed with carbonate solution from the final stabilization the reaction of the waste water in the labyrinth is neutral or slightly acid. Nitroglycerine flows down the sloping base of labyrinth, to be returned to the stabilization process. It is drawn off in the normal way by means of a hose-pipe, avoiding as far as possible, the use of stoneware stop-cocks.

Stabilization of the recovered nitroglycerine consists in washing and filtering

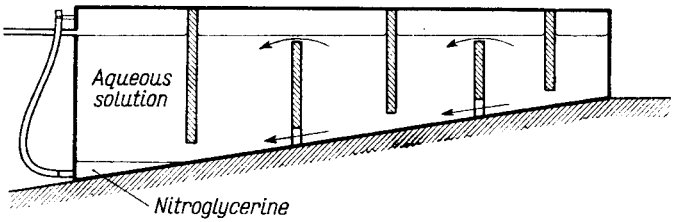

FIG. 25. Diagram of a labyrinth.

by the usual methods. From the stabilization water about 1% of the total nitroglycerine output is recovered.

Water from which the nitroglycerine has separated flows to a tank lined with lime-stone and after being neutralized it is discharged to a river or pool. Attempts have been made to recover the appreciable quantity of ions: $NO_3^{\ominus}$, $SO_4^{2\ominus}$ and $HSO_4^{\ominus}$ still present in the water. In a patent taken out by the Dynamit A.G. in Hamburg [26] neutralization of the waste water with ammonia was suggested followed by evaporation. This yields about 8 kg of nitrates and sulphates mixed in the ratio of approx. 7:3 for every 100 kg of nitroglycerine. It was proposed to use the mixture as a chemical fertilizer.

THE SPENT ACID

After separation of the nitroglycerine, the following remain in the spent acid: nitroglycerine, dinitroglycerine, mixed esters of sulphuric and nitric acid. The two latter esters react slowly with the nitric acid contained in the waste acid to form further nitroglycerine, which floats on the surface of the acid.

There is a further method of obtaining nitroglycerine from the spent acid if the main product is separated immediately after nitrating. Nitration is commonly performed at the temperature of 25–30°C. The waste acid is cooled after nitration is complete, to the temperature of 15°C or less, and as a result a part of the nitroglycerine which was dissolved in the acid is separated.

The amount of nitroglycerine recovered from the spent acid amounts to about 2% of the total output.

The separation rate of this supplementary yield of nitroglycerine depends not only on the velocity of the additional reaction of esterification, but also on the purity of the glycerine used and the purity of the mixed acid. It should be borne in

mind that the separation of nitroglycerine from the spent acid may take several days and that an acid apparently free from nitroglycerine may represent a source of danger. Lengthy contact between nitroglycerine and spent acid may be followed by decomposition. The explosions of nitroglycerine which has risen to the surface of spent acid have been known to occur, chiefly in the summer. On the basis of numerous experiments Oehman, Camera and Cotti [27] have constructed a diagram indicating the composition of spent acid which can be dangerous in contact with nitroglycerine (Fig. 26).

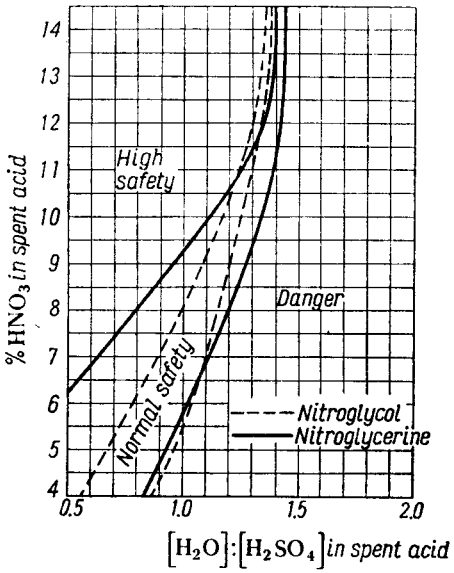

FIG. 26. Safety diagram of acidic nitroglycerine, according to Oehman *et al.* [27]. For comparison, nitroglycol is also indicated.

The supplementary separation is carried on in a special building. Several days' supply of spent acid is collected in special lead tanks (settlers) each having a capacity sufficient to hold the acid collected from a full-day's nitration. Nitroglycerine collected on the surface of the acid may be removed in various ways: by means of an aluminium spoon (the old system) or by displacing the contents of the tank from below with the waste acid (the combined process, p. 95). The handling of waste acid free from nitroglycerine is not wholly safe, since more nitroglycerine may still separate out.

Taking into account only the inorganic components of the spent acid, its composition is as follows:

HNO_3	9–14%
H_2SO_4	70–75%
H_2O	15–17%
sp. gr.	1.74–1.76

In order to make use of the spent acid it must undergo denitration, which consists in separating the nitric acid from the sulphuric acid. The spent acid should be denitrated as soon as possible after the supplementary separation of nitroglycerine.

To lessen the danger of handling the spent acid immediately after the separation of nitroglycerine, the addition of a certain amount of water was suggested by Nathan, Thomson and Rintoul [2]. On dilution with water, the solubility of the nitroglycerine in acid is increased and a loss of nitroglycerine occurs because it no longer separates. However, the method greatly enhances the safety of handling the spent acid and capital costs are reduced since no installation for the supplementary separation of nitroglycerine is required.

Originally 2% of water were added to the spent acid and this prevented the separation of nitroglycerine at temperatures from 10 to 15°C. Nevertheless in 1906 a tank filled with this dilute spent acid exploded while being transported. Further experiments showed that nitroglycerine can separate from acid diluted in that way if its temperature falls below 10°C. Addition of 5% water was therefore introduced, to prevent separation of nitroglycerine even at a temperature of 0°C. At the present time this procedure is widely used with new methods of nitration including continuous processes.

The addition of water to detain nitroglycerine in the spent acid not only increases the solubility of nitroglycerine in the acid, it also alters the equilibrium of the reaction between dinitroglycerine, nitroglycerine and acid in such a way that dinitroglycerine does not undergo further nitration and the trinitrate is not formed (Renner and Helle [28]).

Spent acid from nitroglycerine manufacture is not used to prepare nitrating mixture since it contains too much organic matter with which it is undesirable to contaminate the nitration. Decomposition of these substances during nitration could make the process difficult to control and might lead to accidents.

Generally, therefore, the spent acid remaining after manufacturing nitroglycerine and similar nitric esters undergoes denitration. The spent acid should be stored in lead tanks, and before passing on to the denitration tower, any separated nitroglycerine is skimmed from the surface by means of an aluminium ladle.

The denitrating tower (*1*) (Fig. 27) consists of a steel shell lined with special acid-resistant brick, and is packed with quartz or with Raschig rings of refractory material or of iron with a high silicon content. A distributor at the top of the tower delivers the spent acid in counter-current to superheated steam and air entering at the bottom of the tower via a jet (*2*). A temperature of 300–350°C is maintained inside the tower by means of superheated steam. The steam and air drive off nitric acid and nitric oxides (NO and NO_2) present in the spent acid or formed in the denitrating tower as the result of the oxidation of organic compounds. Denitrated sulphuric acid flows through a syphon outlet (*6*) at the bottom of the tower and is cooled in the tub (*7*) before being concentrated or used for mixing with oleum and nitric acid.

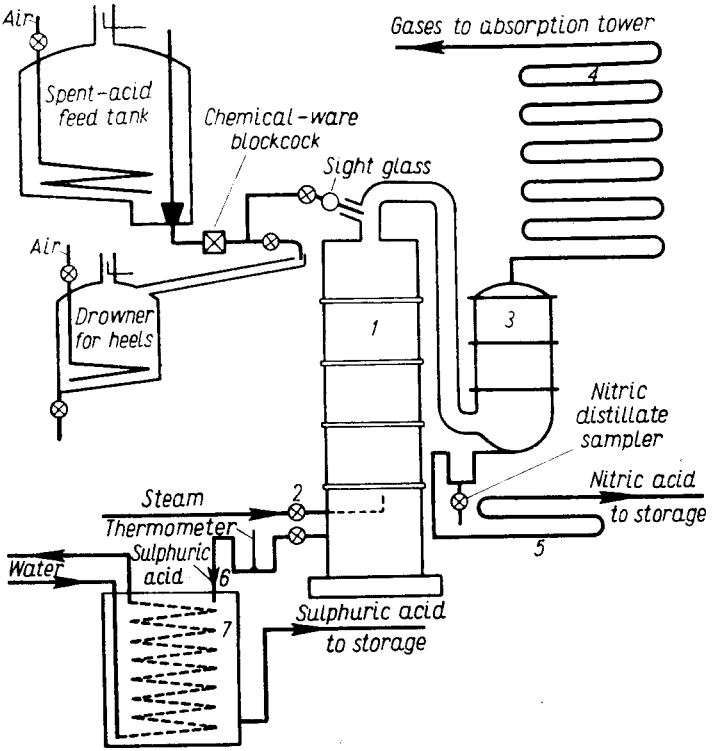

FIG. 27. Recovery (denitration) of spent acid (according to W. de C. Crater [29]).

Nitric acid and nitrogen oxides are driven off together with water vapour and pass from the tower through the top to a "Bleacher" (*3*) filled with disks or cylinders where they pass in counter-current to the condensed acid which returns from the S-bend condenser (*4*) of high-silicon iron to flow through (*5*) to storage.

When nitric acid alone is used for nitration and the product and acid are drowned in hot water or hot dilute nitric acid as in the case of cyclonite manufacture, where no organic substances remain in the acid (all being decomposed), the spent acid is readily recovered by feeding it to an absorption tower in place of part of the water normally added. The acid should be fed in at a point in the tower where the concentration of acid is approximately the same as that of the acid being added.

In a plant of this type nitric acid of about 90% and sulphuric acid of 70% are obtained. In the absorption towers nitric acid of 30–60% is produced.

According to its size a plant for denitrating spent acid may have a daily output from 5 to 25 tons of acid.

The denitration system works satisfactorily only for spent acid from the nitration of glycerine and similar alcohols. In spent acid from trinitrotoluene production the high content of dissolved nitrated hydrocarbons causes an excessive reduction of nitric acid at the top of the denitrating tower. Thus spent acid from the nitration

of hydrocarbons are unsuitable for denitration and are utilized instead by mixing with oleum and concentrated nitric acid (Vol. I, p. 150).

RAW MATERIALS FOR NITROGLYCERINE MANUFACTURE

GLYCERINE

As already mentioned above, the purity of the glycerine exerts a fundamental influence on the efficiency and safety of nitroglycerine manufacture. The so-called dynamite glycerine, a very pure water-free product, distilled several times under reduced pressure is produced for manufacture of nitroglycerine.

Glycerine is obtained mainly by the hydrolysis of fats. During World War I when fats were in short supply in central Europe, glycerine was produced on plant scale by sugar fermentation. Fermentation glycerine is suitable for the manufacture of nitroglycerine although it contains certain by-products not present in glycerine derived from fats, hence the yield of nitroglycerine from fermentation glycerine is somewhat lower than that from glycerine obtained by the hydrolysis of fats. The main by-product in fermentation glycerine is trimethylene glycol (see p. 155), which forms an explosive nitric ester. When it is present the nitration temperature should be kept lower than that normally maintained during nitration of glycerine derived by hydrolysis. During the nitration of fermentation glycerine the temperature should be particularly strictly controlled. Dynamite glycerine is a transparent, highly viscous, colourless, or yellowish or even pale-brown coloured liquid. The intensity of colour is not of critical importance, but light-coloured samples are considered more suitable for nitration than darker ones. Dynamite glycerine usually has a light, distinctive smell resembling that of caramel.

According to the standards applicable in different countries, dynamite glycerine should meet the following requirements:

(1) colour — as pale as possible;

(2) odour — no unpleasent smell should develop on heating to 100°C;

(3) density at 15.6°C — not less than 1.262 g/ml;

(4) reaction neutral;

(5) glycerine content should be at least 98.5–99%, the limiting water content being 1% or in some countries 1.5%;

(6) mineral impurities should not exceed 0.05–0.15%;

(7) maximum content of non-volatile organic substances — not higher than 0.1–0.15%;

(8) it should be free from carbohydrates, proteins and other nitrogen-containing compounds, acrolein, sulphites and sulphides. Sometimes the presence of white arsenic as well as calcium, magnesium or ammonium salts is admissible, but in trace quantity only. Sulphates and chlorides are permitted only in traces e.g. not more than 0.01% calculated as NaCl;

(9) no oils or fats, i.e. glycerides of fatty acids, may be present. In the U.S.A.

standards the admissible amount of fats is equivalent to 0.1% of Na_2O, used as NaOH for hydrolysis. Further no fatty acids should be present.

The most reliable method of determining the quality of glycerine is the laboratory nitrating test. This should be carried out under conditions that correspond as closely as possible to those prevailing in the plant. During the laboratory nitration, temperature, the rate of separation of the nitroglycerine and the acid layers, the contact surface of phases and so on should be recorded.

After separating and washing the products as in large-scale operations the yield is determined. According to the temperature applied this should amount to:

nitrating temperature	yield
30°C	225–226%
15°C	228–229%

For experimental nitration either the Schlegel–Novak apparatus [30] simulating a large scale nitrator or Hofwimmer's nitration burette [31] are usually used. Normal laboratory apparatus with a mechanical stirrer can also be used.

ACIDS

Acids for nitrating glycerine must be as pure as possible. Nitric acid (sp. gr. 1.50) should not contain more than 1% N_2O_4.

Sulphuric acid (sp. gr 1.84) and oleum (20–25%) should be virtually free from lead sulphate which is liable to be present in old installations constructed of lead, and also from sulphates of iron, as these substances hinder the separation of nitroglycerine and acid. Since such acid is not always available storage of sulphuric acid and oleum in special cast iron tanks is recommended in order to allow impurities to settle. Acid is drawn from the upper part of the tank so that the slime composed of iron and lead sulphates remains on the bottom. Similarly, the mixed acid is stored in tanks so designed that the precipitate can collect on the bottom.

BATCH METHODS OF NITROGLYCERINE MANUFACTURE

OLD PROCESSES

The oldest recorded method of manufacturing nitroglycerine was a most primitive process that consisted of dropping small amounts of glycerine, e.g. 350 g, into a cast iron pot containing a mixture of nitric and sulphuric acid. The pot was cooled by standing in a larger, stoneware vessel containing water and ice, and hand stirring was performed with an iron rod. When the nitration was completed (or if danger of decomposition arose) the contents of the cast-iron pot were turned out into the water and ice. Water was then removed by decantation and the blasting oil was washed. In that way a 200% yield of nitroglycerine was obtained.

The design of apparatus to facilitate rapid and efficient removal of the heat produced during nitration was not known at that time. Solution of these difficulties was therefore sought in modification of the manufacturing process itself, as suggested by Boutmy and Faucher [32]. They divided the nitrating process into two

stages. At each stage a certain amount of heat is developed, which is less, of course, than the total heat of nitration.

The stages suggested by Boutmy and Faucher are as follows:

(1) Dissolving glycerine in sulphuric acid to form glyceryl-sulphuric acid.

(2) Adding nitric acid to the solution of glycerine in sulphuric acid.

The greater part of the heat is produced during the relatively safe process (1). The amount of heat developed during nitration proper (2) is therefore relatively small and the temperature can be controlled easily even if primitive methods of cooling are used.

For several years (until 1882) the Boutmy–Faucher method was used in France and Great Britain. In completely primitive apparatus, about 680 kg nitroglycerine were made at a time. The disadvantage of this method was that the nitroglycerine obtained by nitrating according to reaction (2) separated only very slowly from the acid. In the standard method the contents of the nitrator were allowed to stand overnight to permit separation of the nitroglycerine. This lengthy contact between the nitroglycerine and the acid involved the danger of decomposition. Indeed, in factories where this method of nitroglycerine manufacture was practised frequent explosions occurred during the separation stage. Finally this method had to be abandoned and at the present time it is of historical importance only.

NOBEL PROCESS

Nobel invented a radically new design of nitrator for the manufacture of nitroglycerine. Originally it was made of sheet lead and equipped with a cooling coil supplied with water, (Fig. 15, p. 65) and later a water-cooled jacket made of wood was added (Fig. 28). In later versions of the Nobel nitrator the cooling jacket was omitted in favour of a four-fold cooling coil with which it was easier to control the nitration temperature.

Before starting the nitration the cooling coil and the compressed air inflow should be checked to ensure that they are not damaged, and it is also necessary to ensure that the lower discharge stoneware cock is well lubricated with vaseline and that its discharge outlet is situated above the drowning tank. The inlet valve admitting the cooling water to the coil and to the jacket is then opened fully, and through the pipe (*1*) mixed acid is introduced to fill the nitrator to $\frac{1}{2}$–$\frac{2}{3}$ its volume. Afterwards compressed air is introduced by means of three pipes (*2*), (*3*) and (*4*) and then the glycerine pipeline closed by a tap (*5*) and the lever (*6*) is opened. The lever (*6*) is fitted with a spring which closes the cock instantly when the nitration foreman ceases to press the lever.

Glycerine is run into the nitrator through a funnel in the cover. The part of pipe containing (*5*) and (*6*) is joined by means of a hose to the stiff pipe for feeding glycerine.

During nitration the temperature inside the nitrator is measured by thermometers (*7*) and (*8*) and is controlled by the operator who reduces the flow of glycerine if the temperature rises too high. Acid vapours together with the air used for mixing

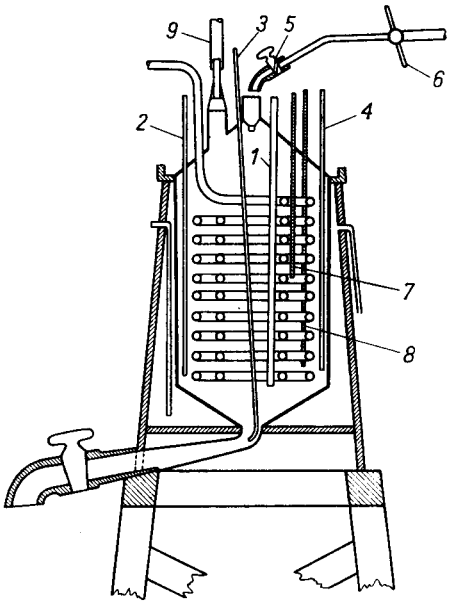

FIG. 28. Nobel nitrator, old pattern.

is removed through the ventilator duct (*9*). The conical cover of the nitrator is equipped with several sight windows through which it is possible to observe the interior of the nitrator.

After a measured amount of nitroglycerine has been introduced the exit of the glycerine supply pipe is pushed as far as possible away from the funnel, and under the lower discharge tap a leaden gutter is attached to permit the contents of the nitrator to flow into a separator. Several minutes after the glycerine feed has been stopped the cooling and then the compressed air supply are interrupted, after which the lower cock is opened immediately to allow the nitroglycerine and acid emulsion to stream via the gutter to the separator (Fig. 29).

The separator is a rectangle-shaped tank with a conical bottom and is made of sheet lead. Its cover, also of lead plate reinforced with lead-coated iron rods, is equipped with a number of windows through which it is possible to observe the liquid surface in the separator. The exhaust duct with a sight glass, and a thermometer are also fitted in the cover. Sometimes a compressed air line is led through the cover to be opened in case the separator contents have to be discharged to the drowning tank. In the lowest part of the separator there is a window (*1*) and three outlet valves: two at the side for acid (*2*) and nitroglycerine (*3*) respectively and one at the bottom leading to the drowning tank (*4*). While the separator is being filled and during the separation process the tap (*4*) is connected with the drowning tank. At the side of the separator, slightly higher than the separation line between the nitroglycerine and acid phases, a cock (*5*) is fitted for discharging the nitroglycerine into the primary washing tank (*6*). The level at which the cock (*5*) is fitted is

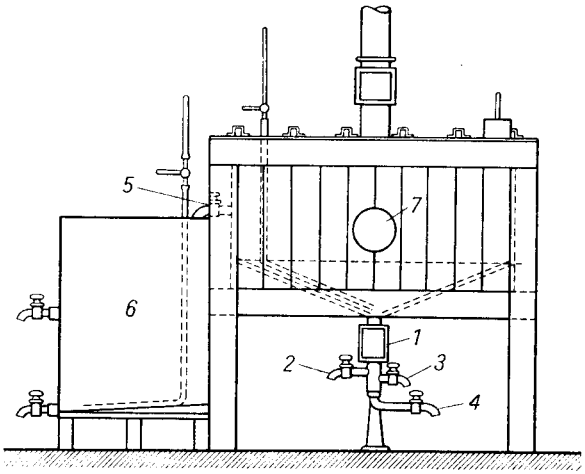

FIG. 29. Nobel separator (Naoúm (11]).

determined accurately by calculation of the charge and of the nitroglycerine yield from one nitrator.

When through the sight glass (*7*) a distinctly clear separation line is visible between the phases, the main yield of nitroglycerine is removed by means of the cock (*5*). Then acid is discharged through the tap (*2*) to leaden settling tanks situated in another room. The separation surface of the two phases is observed through the window (*1*) so that the tap (*2*) can be closed at the right time and the cock (*3*) opened. The amount of nitroglycerine discharged via the tap (*3*) is added to the main yield of nitroglycerine in the washing tank (*6*).

After-separators wherein the waste acid is stored, are open tanks of lead. Nitroglycerine that collects on the surface is removed every few hours with an aluminium ladle, and is to be poured into the preliminary drowning tank situated in the same room.

After the primary washing nitroglycerine is transferred to the final washing by the usual methods. The solutions and water remaining after washing are transferred to the labyrinth. The flow-sheet is shown in Fig. 30 and a complete view of the plant is given in Fig. 31.

NATHAN, THOMSON AND RINTOUL PROCESS

As compared with the Nobel process for nitroglycerine manufacture certain innovations were introduced in this method, namely:

(1) new design of the nitrator;

(2) use of the nitrator as a separator;

(3) omission of nitroglycerine discharge cocks connecting the separator to the washer;

(4) abandoning the additional recovery of nitroglycerine from the spent acid and hence the elimination of settling tanks.

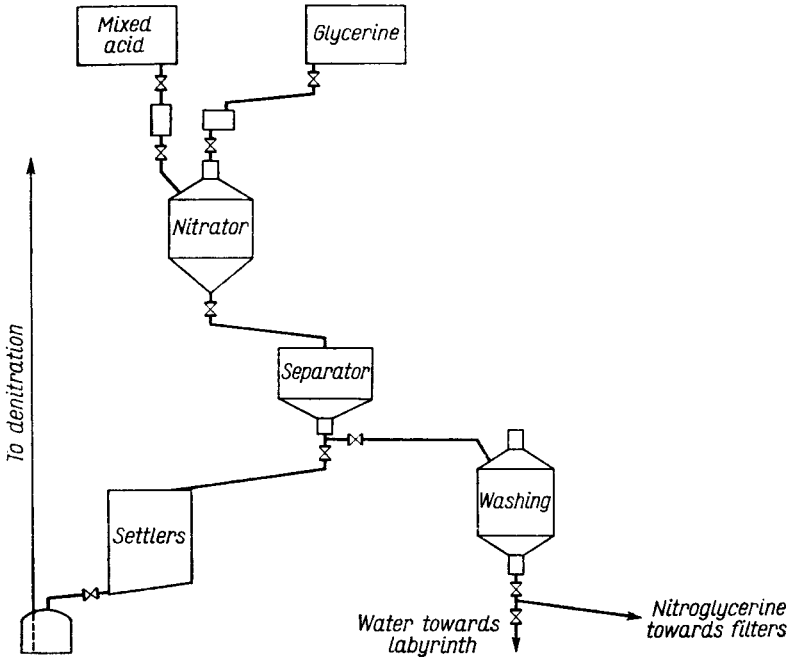

FIG. 30. Flow-sheet of Nobel system of manufacture of nitroglycerine.

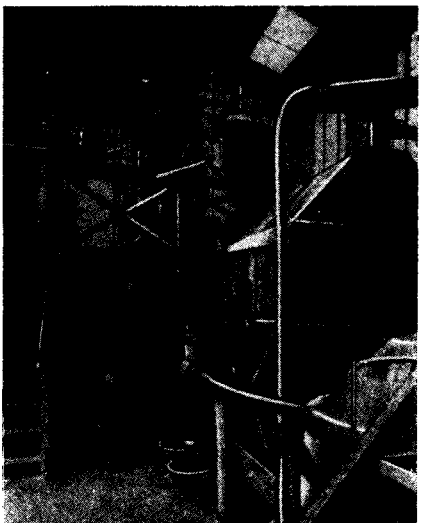

FIG. 31. General view of nitrator, separator and pre-wash tank, Nobel system (Naoúm [11]).

The nitrator–separator used in the Nathan, Thomson and Rintoul process is a cylindrical vessel with a conical cover carrying a small chimney (Fig. 32).

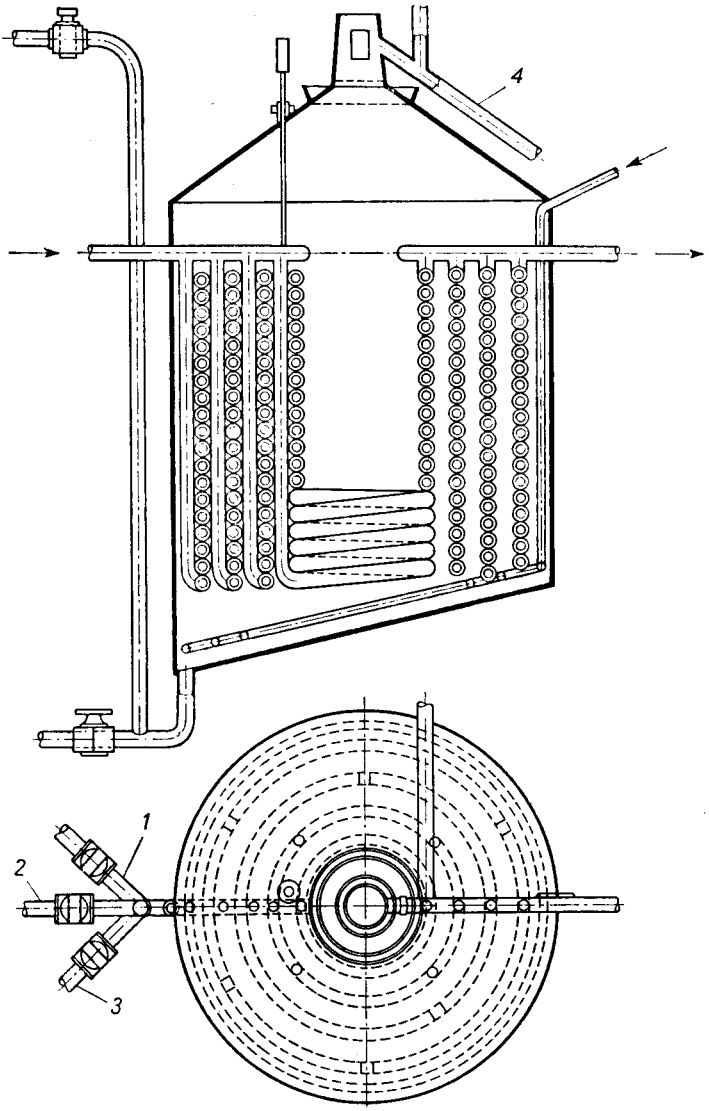

FIG. 32. Nitrator–separator of Nathan, Thomson, Rintoul [2].

The cover, the chimney and the cylindrical part of the nitrator are fitted with sight glasses so that it is possible to watch the nitrator contents. The bottom of the vessel slopes downwards at one side. Inside the nitrator there is a four-fold cooling coil, a compressed air pipe connected to the bottom, and two thermometers (one of the two visible in the drawing). The lowest part of the nitrator is connected with a duct that branches into three pipes (*1*, *2*, *3*). Pipe (*1*) is used for removing the spent acid to denitration, after the separation of nitroglycerine is complete. Pipe (*2*) allows the nitrator contents to be discharged into the drowning tank. Pipe (*3*) has two branches leading to the acid tanks situated above the nitration house. One of these tanks

holds nitrating mixture and the other spent acid. Spent acid is used to displace the nitroglycerine layer through the overflow (4) in the upper part of the nitrator. In order to avoid any leakage of nitroglycerine from the nitrator to pipe (*3*), for instance during stirring, the three-way discharge pipe is kinked at a point about 30 cm below the lowest part of the nitrator. Nitroglycerine is discharged from the nitrator through the overflow (*4*). Acid vapours are drawn off through the chimney by means of an exhauster fan.

In the nitration house two nitrators are situated with the primary washing tank between them (Fig. 33).

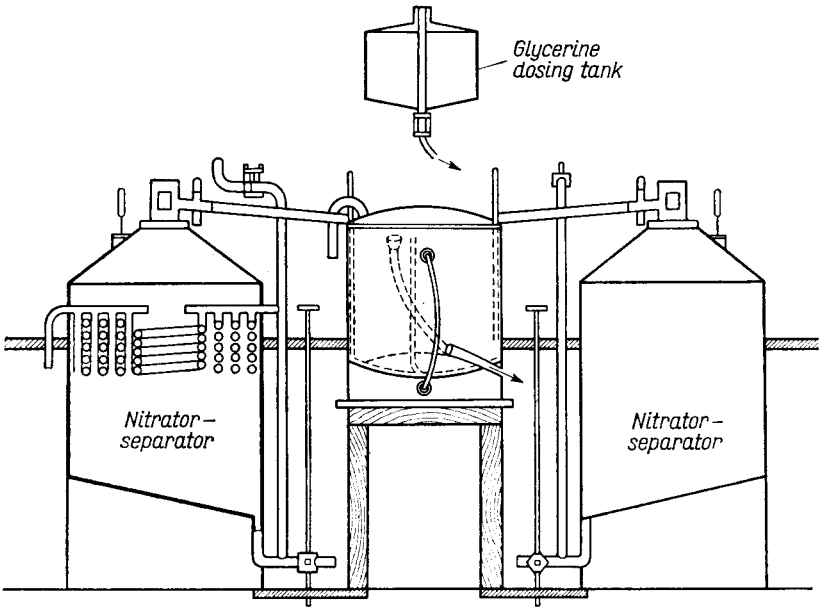

FIG. 33. A unit composed of two nitrator–separators and pre-wash tank.

The course of nitration is as follows: the nitrator is fed with the mixed acid Then the cooling water and compressed air lines are opened and glycerine is forced through the nitrator chimney in the form of a spray by means of compressed air. When the whole of the glycerine has been introduced into the nitrator its contents are stirred for a certain time and then the cooling water inlet is closed and stirring is stopped. The suspension is allowed to stand in the nitrator until the nitroglycerine has separated, the progress of separation being watched through the inspection window. Water is then added to prevent further separation of nitroglycerine.

When the separation is complete spent acid is introduced upwards into the nitrator through the pipe (*3*) to displace the nitroglycerine, the latter passing through the overflow (*4*) into a washer filled with cold water stirred by means of compressed air. There are some plants where the separation of nitroglycerine and acid is repeated after a lapse of at least 2 hr after the end of nitration, water then being added as described below. When the nitroglycerine has been removed from

the nitrator part of the spent acid (about $\frac{1}{5}$ of the nitrator's capacity) is discharged to a pressure-egg situated beneath the nitrator, the water inlet to the cooling coil is opened again and stirring with compressed air is renewed in order to cool the spent acid to 15°C or less, 5% of water being added through the nitrator chimney. The temperature of the acid is increased approximately by 3°C for 1% water. The acid is cooled to about 15°C and transferred via the pipe (*1*) to the tank below the nitrator, when it goes to the denitration process. Sometimes a certain amount of nitroglycerine is separated from the dilute acid on cooling. This should be discharged to the washer by displacement with spent acid as already described.

While one of the nitrators is in use as a separator, nitration is carried out in the other one and vice versa thus maintaining uninterrupted operation.

The nitroglycerine, washed twice with cold water, is then transferred to the final purification stage in another building and the wash water is transferred to the labyrinth in the usual way.

According to British reports from World War I [33], during nitroglycerine manufacture the nitrogen content of the nitric acid (including that recovered by denitration) was consumed as follows:

95.6% chemically combined in nitroglycerine
4.0% lost during nitration
0.4% lost during denitration

COMBINED PROCESS

The method of Nathan, Thomson, and Rintoul was used only in a few factories and generally on the Continent a combined process incorporating the advantages of the Nobel process with those of the Nathan, Thomson and Rintoul process was used.

In this arrangement the nitrator–separator of the Nathan system was combined with settlers of improved design so as to achieve a more precise separation of the nitroglycerine and spent acid. This settler is reminiscent of the Nathan nitrator (Figs. 34 and 35).

It comprises a cylindrical vat with a conical cover with which a glazed or glass

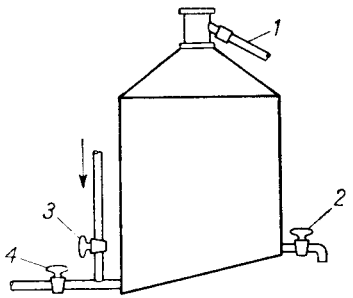

FIG. 34. Spent acid after separating tank (settler) in the combined method.

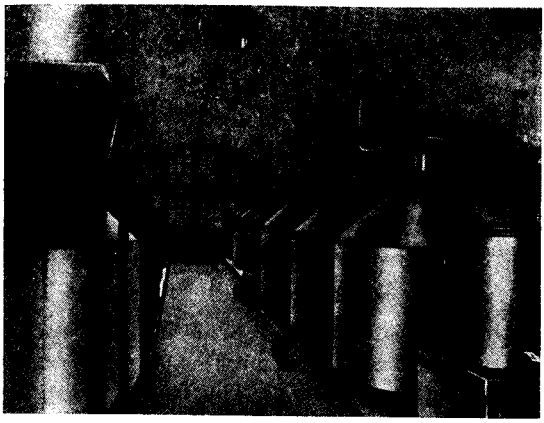

FIG. 35. General view of a battery of secondary separation tanks (Naoúm [11]).

chimney with a small duct (*1*) is connected, made of a down-bent pipe. Spent acid from the nitrator–separator is run into the settler through a pipe in its cover. The bottom is sloping and to its lowest part a pipe is connected through which spent acid can be led to the settler from a high-level tank by means of the cock (*3*). Another branch of this pipe permits the contents of settler to be discharged if the valve (*4*) is opened. The capacity of each settler is large enough to contain the full day's output of one nitrator. A flow-sheet is given on Fig. 36.

After nitration is completed, the contents of the nitrator are allowed to stand

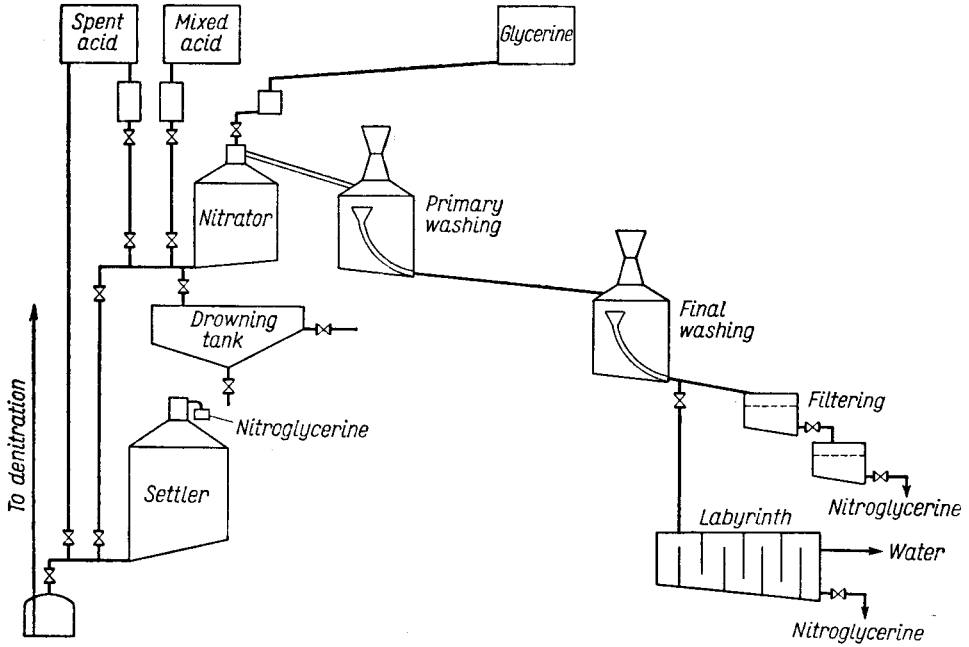

FIG. 36. Flow-sheet of the combined method of nitroglycerine manufacture.

quietly while the other nitrator comes into operation. When the layers of nitroglycerine and acid have separated, spent acid is introduced into the bottom of the nitrator–separator from the upper waste acid tank to displace the nitroglycerine which is transferred for primary washing. The spent acid free from nitroglycerine, after passing through a transit tank, flows to the settlers. At intervals of a few hours nitroglycerine collecting on the surface of acid is displaced by means of spent acid flowing down from the upper tank and into the settler from below. The overflowing nitroglycerine passes through a gutter to an aluminium vessel. By repeating this operation every few hours lengthy contact between the nitroglycerine and the acid, which involves the risk of nitroglycerine decomposition, is avoided. Separation of nitroglycerine is almost 100% and of course the safety of the operation is considerably increased.

In one of German plants in which this method was used the following materials balance based on the average of a years' production, was achieved:

From 100 parts by weight of glycerine, 228.7 parts by weight of nitroglycerine were obtained.

Consumption of glycerine:

94.1% converted to nitroglycerine passed directly to filtration,
3.0% converted to nitroglycerine recovered from the spent acid,
0.8% converted to nitroglycerine recovered from the wash waters.
Total yield was 97.7%.

2.1% of glycerine was lost.

Consumption of nitric acid:

For 100 parts by weight of glycerine, altogether 261 parts by weight of nitric acid were used, whereof:

74.0% were combined to form nitroglycerine,

17.8% were recovered in the denitration process,

8.2% represent losses (of which the washing water accounted to 7.3%, and the denitration process 0.9%).

Consumption of sulphuric acid:

For 100 parts by weight of glycerine, 314.5 parts by weight of H_2SO_4 were used, whereof:

99% were recovered in the denitration process, 1% was lost.

CONTINUOUS METHODS OF NITROGLYCERINE MANUFACTURE

The manufacture of nitroglycerine is one of the most dangerous operations in the whole explosives industry, due to the high sensitiveness of nitroglycerine to impact and friction and its ability to burn to detonation. The decomposition of nitroglycerine can readily be induced by autocatalytic chemical decomposition in contact with mineral acids.

All this makes the manufacture of nitroglycerine particularly dangerous and all that has been said previously with regard to the danger of TNT manufacture and the advisability of producing it by continuous methods applies with much greater emphasis to nitroglycerine.

Continuous nitration of glycerine was suggested as early as 1866 by Nobel [8] who mixed the two reactants by pouring them through a perforated funnel, and by Rudberg [34]. The latter system was in limited operation for a short time. The nitrator is shown diagrammatically in Fig. 37. It comprised a lead trough (*1*) with a step shaped bottom, to which cooling was applied, in the form of a stream of cold water,

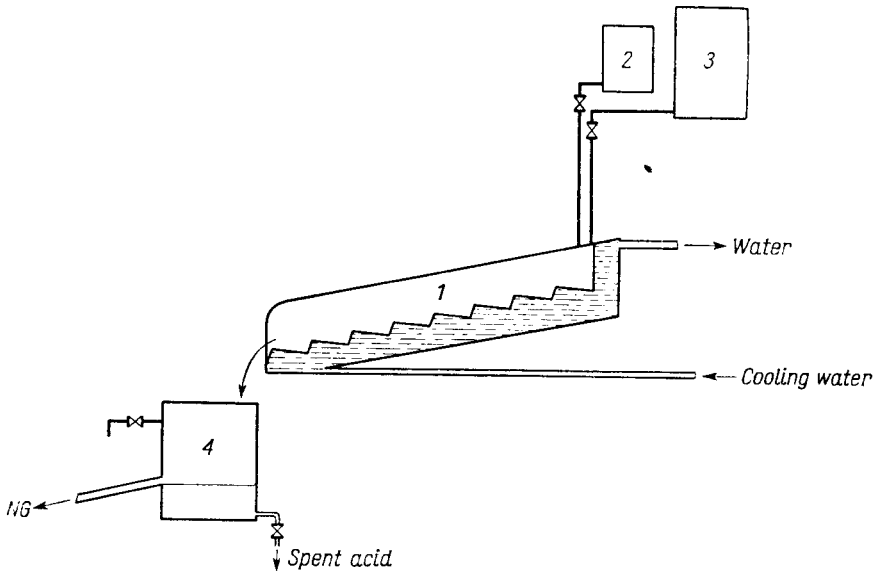

FIG. 37. Continuous nitration of nitroglycerine according to Rudberg: *1*—nitrator, *2*—glycerine, *3*—mixed acid, *4*—separator.

to maintain a temperature below 30°C. Two streams: one of glycerine from a container (*2*) and the other of mixed acid from (*3*) were introduced into the nitrator. Reaction occurred as they flowed down into a tub (*4*) filled with water. Nitroglycerine was collected through an overflow.

Two patents for the continuous nitration of glycerine by Kurtz appeared in 1878–1879 [35] and other methods comprising a continuous manufacturing scheme where glycerine and nitrating acid were mixed in a spraying nozzle were patented by Maxim in 1891 [36] and Evers in 1902 [37]. These ideas were incorporated into the modern plants (p. 114).

However, largely because of doubts about the safety of the innovations proposed, they have not found acceptance and it was not until 1927 when the Schmid process was devised and 1935, when the Biazzi process was developed that these continuous production processes were recognized as efficient and safe.

SCHMID PROCESS

The continuous method of nitroglycerine manufacture invented by A. Schmid [38] involves not only continuous nitration, but also continuous separation and washing of the product. A novel idea introduced by Schmid was the nitrator made of acid-resistant steel with mechanical stirring (Fig. 38).

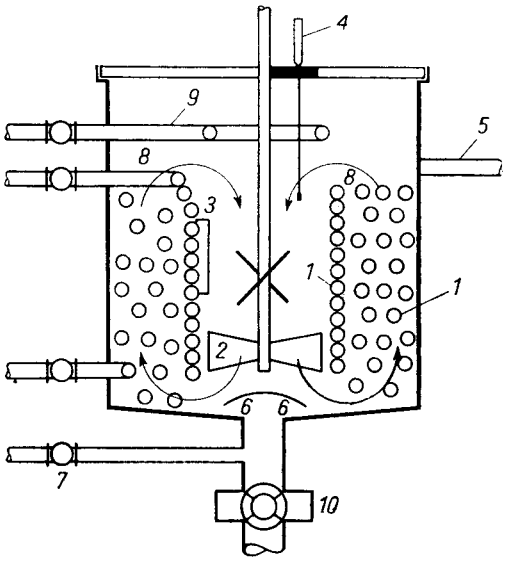

FIG. 38. Nitrator for continuous nitroglycerine manufacture according to Schmid (original pattern).

The nitrator is constructed of acid-resistant steel and equipped with refrigerating coils (*1*) (a baffle formed by the coil separates the interior of the nitrator from the cooled section). Their cooling surface is four times larger than in the usual nitrators, thus cooling is efficient in spite of the high flow rate of the liquid. The propellers of the mechanical stirrer (*2*) revolving at a speed of 200–300 revolutions per minute, extend to within 0.5–1.0 cm of the coils. Above the propellers steel plates (*3*) parallel to the axis of the nitrator are fixed to promote a better circulation of liquid. It is also possible to attach above the main propellers (*2*) another pair of smaller ones acting in the opposite direction. In the cover a sight glass and a thermometer (*4*) are installed. Due to the high flow velocity of the liquid during nitration the thermometer must be protected by a metal sheath.

Before nitration starts, the nitrator is filled with spent acid up to the level of the overflow (*5*). The water inlet to the cooling coils is opened, the stirrer is set in motion, and through pipes (*6*) and (*7*) fresh mixed acid is introduced to be carried off with the stream of liquid and blended with the spent acid. Mixing takes place without any notable thermal effect. Part of the liquid is recirculated via the pipe (*8*) and part is run through the overflow (*5*) to a separator. Glycerine enters through the

pipe (*9*) in one or several streams. Should decomposition of the nitroglycerine occur the contents of nitrator are discharged through a valve (*10*) into a drowning tank.

For efficient operation, a steady supply of glycerine and acid at a pre-determined, constant ratio is necessary. The raw materials are delivered by means of pumps driven by a common motor and regulated in such way that a constant relation is established governing the quantity of liquid pumped. The pumps are placed in an auxiliary room above the nitration house. Further tanks for glycerine and mixed acid are located in the same room.

Due to the high velocity of stirring and to the large cooling surface the output of this nitrator is about 10 times larger than that of conventional nitrators of the same capacity.

An improvement to the Schmid nitrator has been introduced by Nauckhoff [25]. He replaced the cooling coils by a tubular cooler (Fig. 39).

In the separator for continuous separation of nitroglycerine and acid originally used in the Schmid process, certain faults were detected, which were later eliminated in a new design of 1928 (Fig. 40).

The separator, made of acid-resistant sheet-steel, resembles an inclined cylinder and its method of operation is as follows. The emulsion from the nitrator enters through the conduit (*1*). To facilitate the separation of acid and nitroglycerine baffles (*4*) of corrugated steel sheets and a cooling jacket (*5*) are installed. The spent acid is collected in the lower region to form the layer (*2*) while nitroglycerine collects in the upper part of the separator as the layer (*3*). Nitroglycerine is removed continually through the outflow (*6*) while the spent acid is discharged from below over the siphon (*7*), which is a situated at the same level as pipe (*6*).

A general view of a nitrator and separator is given in Fig. 41.

Washing nitroglycerine. According to the Schmid process the continuous washing of nitroglycerine is carried out in towers made of cylindrical glass segments carrying perforated plates shelves of stainless steel between the segments (Fig. 42). All is strengthened on the outside by means of steel rods. Washing towers can also be constructed of stainless steel. An air outlet is connected to the cover of the tower.

Nitroglycerine leaving the separator enters an injector fed with water or with a solution of sodium carbonate or of ammonia, to form an emulsion which flows into the tower from below. Compressed air is also introduced to facilitate mixing and the shelves are also intended to ensure thorough mixing of the emulsion. The latter rises to flow through a siphon pipe into a separator. The separator is built of wood impregnated with paraffin, or of sheet aluminium. It is fitted out with several baffle plates and its construction resembles that of a labyrinth (see Fig. 22). Here the emulsion forms separate layers. Water flows out through the upper siphon pipe, and nitroglycerine through the lower one.

For washing, two towers are usually used: one in which the nitroglycerine is washed with water, the other for washing with sodium carbonate solution or with dilute aqueous ammonia.

In a small plant equipped with a nitrator of 25 l. capacity yielding about 100 kg of nitroglycerine per hour, towers of the following dimensions are used: for water washing the diameter is 0.2 m, and the height 2 m; for alkaline washing the diameter is 0.3 m and the height 2.5 m.

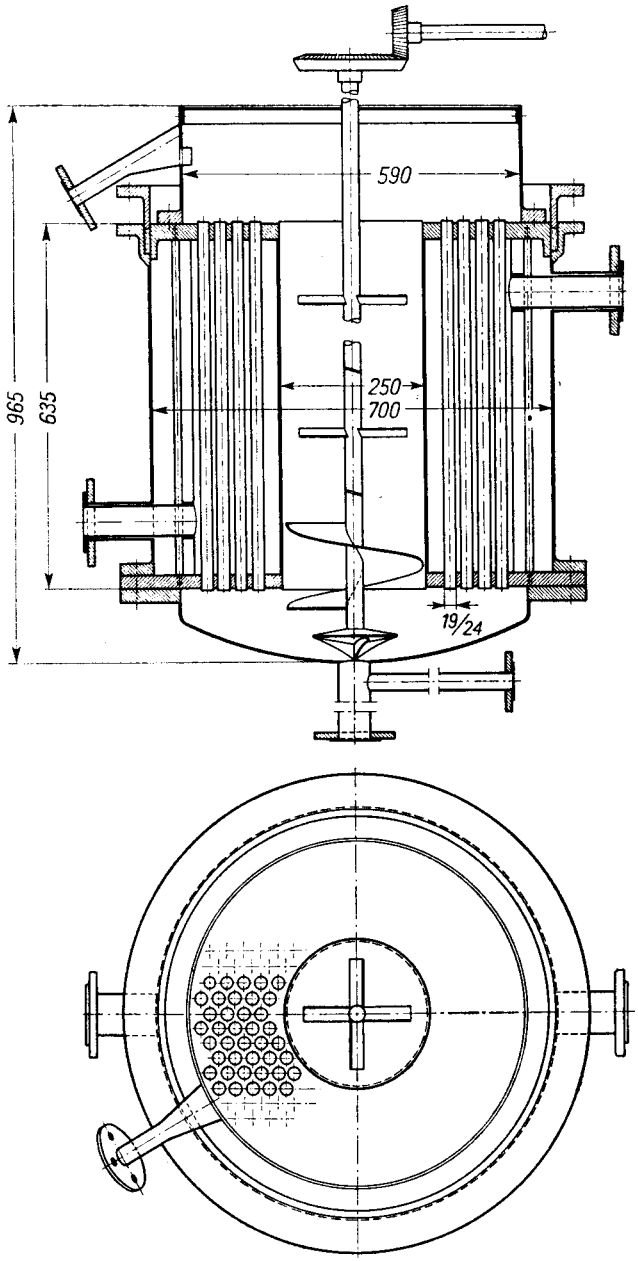

FIG. 39. Nitrator for continuous manufacture of nitroglycerine according to Schmid, improved pattern with tubular cooler by Nauckhoff (Nauckhoff and Bergström [7]).

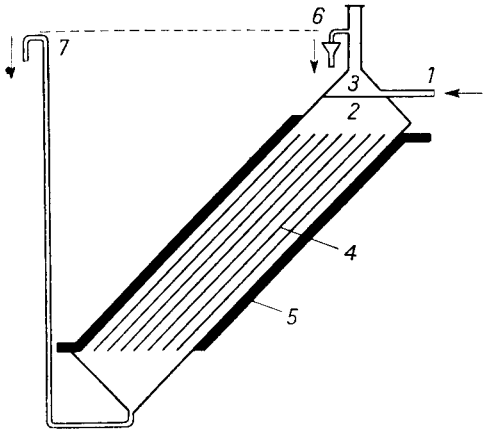

FIG. 40. Continuous separator according to Schmid.

FIG. 41. Schmid nitrator (centre) and separator (left) in Nitroglycerine Aktiebolaget, Gyttorp, Sweden.

A flow-sheet for nitroglycerine manufacture by the continuous Schmid method is shown in Fig. 43.

The whole apparatus is usually located in one room so as to facilitate supervision of the operation. During continuous manufacture the amount of nitroglycerine present in the apparatus is several times smaller (4–5 times) than that in common methods of batch nitrating. The purified product is removed from the column 30–45 min after nitration begins, whereas in existing batch processes nitroglycerine washing does not take place earlier than 2 hr after the start of nitration. The manufacture of nitroglycerine by the continuous method is therefore safer and its safety is further increased, since long pipelines for carrying acid contaminated with nitroglycerine are eliminated, and nitroglycerine passes through the valves in an emulsified form only so that handling of such cocks is less hazardous.

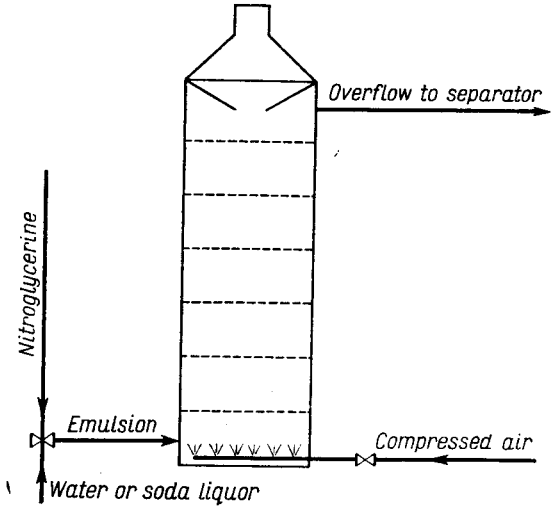

FIG. 42. Continuous washing of nitroglycerine according to Schmid.

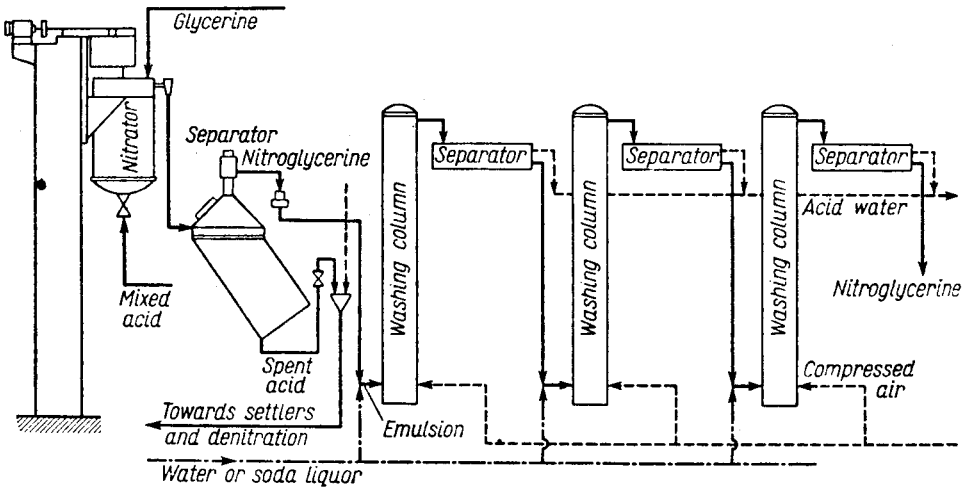

FIG. 43. Flow-sheet of continuous manufacture of nitroglycerine according to Schmid.

Some data published by Stettbacher [39] concerning the Schmid plant at Gyttorp' Sweden, which had a production capacity of 600 kg nitroglycerine per hour are listed below:

capacity of nitrator	75 l.
cooling surface	15 m^2
temperature of the cooling liquid	+10°C
nitrating temperature	+18°C
composition of mixed acid	50% HNO_3+50% H_2SO_4
glycerine to acid ratio	1:5
yield	231.5%

SCHMID–MEISSNER PROCESS

The process invented by Schmid and improved and developed by Meissner [40] has since been adopted in many factories. A distinctive feature of the improved method consists in the extensive use of metering devices and rotameters.

A diagram of the plant is illustrated in Fig. 44. It operates as follows. Nitrating acid filtered through a ceramic filter (*1*) is transferred by compressed air from tanks (*2*) and (*3*) over a rotameter into the nitrator (*14*). Glycerine heated in the heater (*9*) is transported by means of the pump (*10*) through a bronze mesh filter (*11*) to the metering tank (*12*) from which it is discharged by a pressure controlled on the board (*16*). In order to permit the use of a rotameter for metering the glycerine a temperature of 40°C is maintained in the glycerine feed tank, so that no variation in viscosity occurs which would otherwise prevent the use of a rotameter. From the compressed air tank (*13*) an air pressure of about 1.5 atm is applied to both the glycerine and the mixed acid contained in measuring tanks. Thus the glycerine and acid are delivered under the same pressure and any changes in the pressure applied to the raw materials are the same for both liquids.

Nitroglycerine is discharged from the separator (*17*) through an overflow (*17a*) and passing through injectors (*22c*) (*23c*), (*24c*) it enters in turn the washing columns (*22*), (*23*) and (*24*).

In the earlier design when the plant was started up, the first nitroglycerine produced may be polluted by slime from the nitrator and separator. It is therefore transferred to a "hand" washer (*17b*) to be washed as in batch production.

In more modern designs there is no slime in the nitrator and separator as the whole installation is constructed of high-grade acid-resistant steel. The washing tank is maintained, however, in order to wash the residue of nitroglycerine remaining in the separator when the installation is shut down.

To the separator, an overflow for spent acid (*18a*) is fitted, by means of which the height of the boundary layer between the two liquid phases can be regulated. Spent acid flows down to a pressure-egg (*19*), from which it is discharged by means of compressed air to a tank (*18*) (only a part of the pipe is shown) and then to setling tanks as in the combined process, (p. 95).

Columns for nitroglycerine washing are built of glass rings of 200–300 mm diameter, resting on acid-resistant steel plates. Into the first column (*22*) an emulsion of nitroglycerine with cold water produced in the injector (*22c*) is introduced from below. The temperature inside the column is shown by a remote thermometer (*22b*). In the second column (*23*) the washing is carried out in an identical manner except that a warm 3% sodium carbonate solution is used here, while in the third column (*24*) warm water is used to remove sodium carbonate from the nitroglycerine.

The primary separation of nitroglycerine from water or sodium carbonate solution is performed in separators (*22a*), (*23a*) and (*24a*). The lower parts of these columns and separators are equipped with cocks by means of which the residue of nitroglycerine remaining after a shut down is removed together with an aqueous

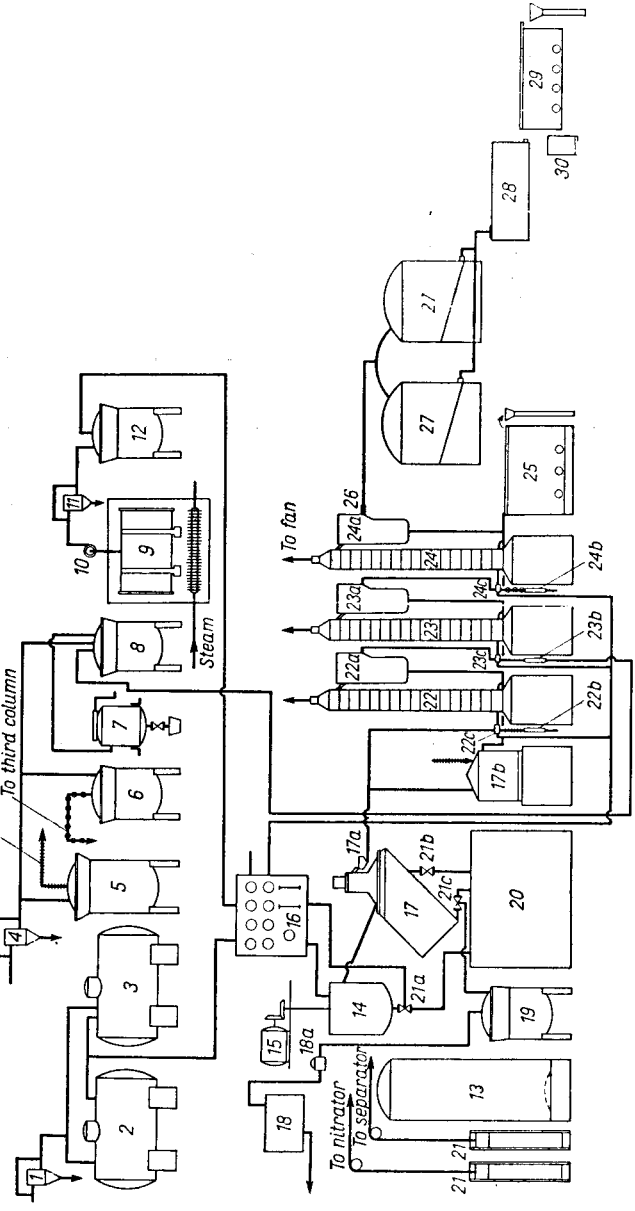

FIG. 44. Flow-sheet of continuous production of nitroglycerine according to Schmid-Meissner: *1*—ceramic filter, *2,3*—measuring tanks for nitrating mixture, *4,11*—bronze mesh filters, *5*—cold water tank, *6*—warm water tank, *7*—sodium carbonate container, *8*—sodium carbonate storage tank, *9*—glycerine warming container, *10*—glycerine pump, *12*—glycerine measuring tank, *13*—compressed air, *14*—nitrator, *15*—motor driving the stirrer in the nitrator, *16*—control panel connected with acid rotameter, reduction valve and distance-thermometer in the pre-washing vat *17b*, *17*— separator, *17a*—nitroglycerine over-flow, *17b*—pre-washing vat, *18*—spent acid tank, *18a*—nitroglycerine over-flow, *19*—pressure egg, *20*—emergency drowning tank, *21*—electric release of safety valves, *21a, b, c*—valves to the drowning tank: (*a*) from the nitrator, (*b, c*) from the separator, *22, 23, 24*—washing columns, *22a, 23a, 24a*—separators, of nitroglycerine from wash-water, *22b, 23b, 24b*—rotameters, *22c, 23c, 24*—injectors emulsifying nitroglycerine with water or sodium carbonate solution, *25*—labyrinth, *26*—injectors for stabilized nitroglycerine, *27*—tanks separators, *28*—nitroglycerine filter, *29*—labyrinth, *30*—nitroglycerine can.

solution or water to a labyrinth (*25*). Nitroglycerine collects here to be sent to a washer (*17b*).

Through the injector (*26*) and by means of rubber pipes nitroglycerine stabilized with an extermely dilute solution of sodium carbonate is transferred to the separating tanks (*27*) wherein the final separation of the emulsion into layers is accomplished. Nitroglycerine is passed through a filter (*28*), whilst the aqueous layer flows down into the labyrinth (*29*). The product removed from the labyrinth is stabilized in the washing tank (*17b*).

RACZYŃSKI PROCESS

The distinctive feature of the process invented by Raczyński [41] is exact metering of mixed acid and glycerine by means of automatic mechanical devices.

The nitrating acid is metered by means of tipping vessel fixed on a horizontal shaft (Fig. 45a).

Acid flows into the vessel (*1*) from a pipe ending inside a container constructed of acid-resistant steel or lead, in which the tipping vessel is located. The stream of acid fills the vessel, and as a determined weight is reached it tips over and another

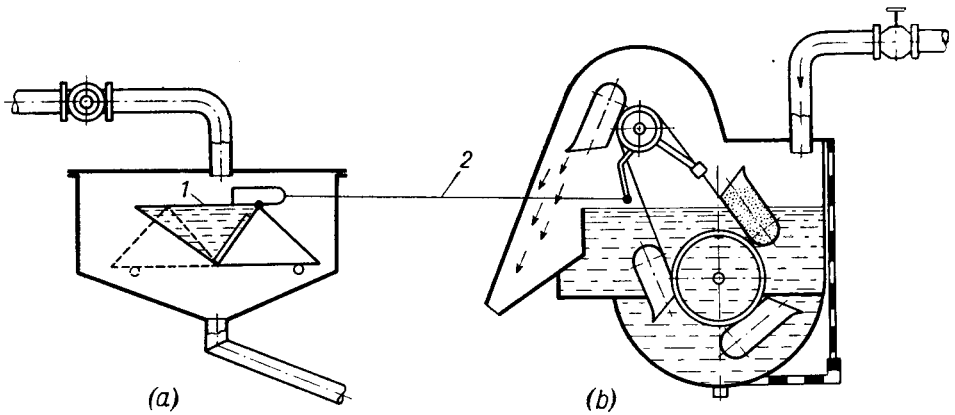

FIG. 45. Apparature for continuous dosage of acid (*a*) and glycerine (*b*) according to Raczyński [41].

empty vessel swings into place under the acid inlet pipe. This fills in turn and tips over to pour off its contents and so the cycle continues. A volume-meter connected to the equipment indicates the volume of liquid measured out. Acid from this device passes into the nitrator.

Glycerine is metered by means of a bucket conveyer (Fig. 45b) driven by hydraulic turbine.

The arrangements for introducing measured quantities of acid and glycerine are connected by a lever (*2*) in such a way that the influx of acid and nitroglycerine into the nitrator proceeds at a pre-determined ratio. Movement of the tipping vessel exerts a pull on the lever and this takes the brakes off the bucket conveyer. At once the conveyer starts to move and continues to do so until the acid metering vessel returns the lever to its former position and stops the conveyer again.

A diagram of a plant for nitroglycerine manufacture by the continuous Raczyński process, including the separating and washing units, is outlined in Fig. 46.

For nitration a nitrator (*1*) equipped with cooling coils and a mechanical stirrer comprising a cylindrical rotor equipped internally with turbine paddles is used. At a sufficiently high rate of rotation, the liquid flows rapidly through the rotor in one direction thus ensuring correct circulation between the coils.

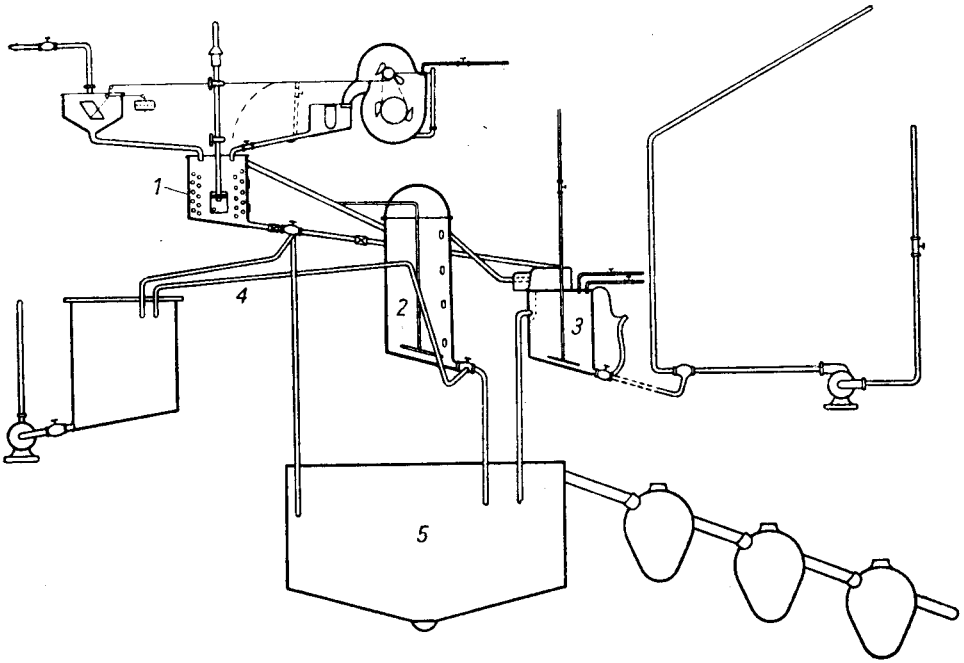

FIG. 46. Flow-sheet of continuous method of manufacture of nitroglycerine according to Raczyński [41].

The emulsion of nitroglycerine and acid flows to a cylindrical separator (*2*) from which the upper nitroglycerine layer flows over the high level pipeline to a primary washing tank (*3*). The spent acid is removed from below by a hydraulic system (*4*). Should any danger of decomposition arise it is possible to empty the contents of the nitrator or separator into the drowning tank (*5*). As the separator is emptied the compressed air inlet valve should be opened simultaneously to mix the nitroglycerine with the acid again.

BIAZZI PROCESS

An original version of the continuous process worked out by Biazzi (Vevey, Switzerland since 1935) [42] includes a new type of acid-resistant steel nitrator (Fig. 47) and the application of "tangential" separators, the liquid content of which is constantly in motion.

One of the first plants nitrating glycerine by the Biazzi process was in operation at Schlebusch in Germany [43]. For a plant with a rated output of 800–1000 kg nitroglycerine per hour a nitrator of 250 l. capacity was used.

The flow sheet of a more modern Biazzi automatic plant is given in Fig. 48.

According to the original description [44] glycerine and glycol are pumped to an intermediate tank (*13*).

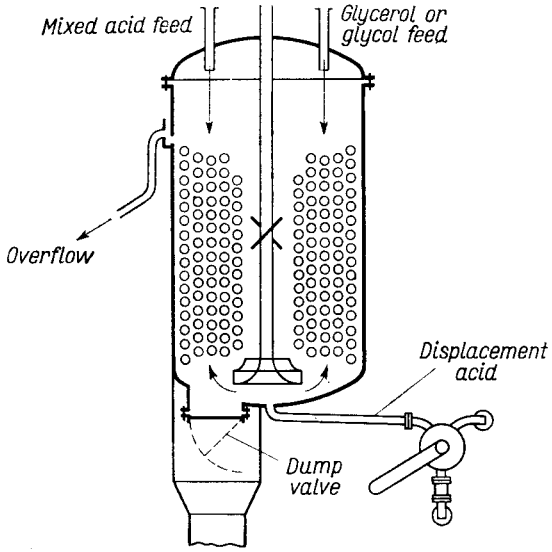

FIG. 47. Continuous nitrator for Biazzi nitroglycerine manufacture (according to Kuhn, W. J. Taylor, Groggins [4]).

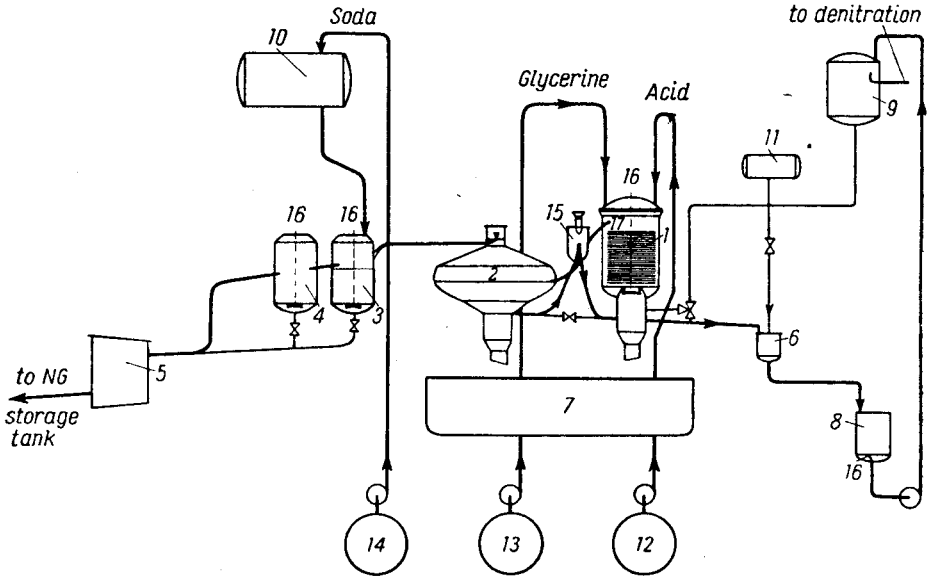

FIG. 48. Flow-sheet for nitroglycerine manufacture according to Biazzi (Stettbacher [45]).

A metering pump introduces the required quantity of glycerine to the nitrator.

The mixed acid (*12*), brought to the nitration house by means of a centrifugal pump, is fed into the nitrator via a metering pump. The flow of the two reacting liquids is maintained in the correct proportion by means of speed controller.

A high speed stirrer (*ca.* 600 r.p.m.) [45] emulsifies the content of the nitrator (*1*).

The temperature in the nitrator is kept within 10–15°C by cooling coils fed with cold water, brine (−5°C) or freon [45, 46]. The temperature is kept constant by means of a thermostatically controlled valve,

The suspension of nitroglycerine in acid flows from the nitrator to acid-resistant steel separator (*2*). The separator inlet enters the vessel tangentially about 0.6 m below the nitrator outlet. The separator itself is a shallow cylindrical vessel having a large diameter which is nearly twice as big as that of the nitrator. Its upper part is conical, topped with a cylindrical chimney.

A stream of emulsion enters the separator to meet the emulsion already present there. Above the emulsion there is a nitroglycerine layer, and below it an acid layer. Owing to the tangential direction of flow, the emulsion circulates slowly with respect to the two stationary layers already separated. Since the diameter of the separator is large this rotary movement is extremely slow (peripheral rate of 2–3 cm/sec) and therefore favourable for the agglomeration of small drops of both liquid phases. According to the data contained in Biazzi's patent, by this system separation is accomplished in a time not longer than 10 min.

The temperature inside the separator is determined by means of thermometers situated at two levels: the upper one in the separated nitroglycerine and the lower one in the acid layer. The separator is equipped with a sight glasses through which the boundary line of the liquid phases can be observed.

The spent acid leaves the separator from below to flow via a siphon, the height of which can be automatically controlled, to a diluter (*6*) where 1–2% water is added and then to a spent acid mixer (*8*). Dilute spent acid is pumped to tank (*9*), and is used for displacement of nitroglycerine from the nitrator and separator after nitration has finished. Most of the dilute acid is sent to denitration.

Acid nitroglycerine flows into a battery of stainless steel continuous washing tanks (*3*) and (*4*) provided with stirrers (580 r.p.m.). The first tank (*3*) is fed with 12% sodium carbonate solution. This is one of the characteristic features of the Biazzi process and represents a radical change in approach to the stabilization of nitroglycerine since for the first time the acid nitroglycerine is treated directly with sodium carbonate solution without previous water washing. The heat of neutralization in tank (*3*) is removed by means of a water cooling jacket.

This direct neutralization has the advantage of eliminating the appreciable loss of the nitroglycerine which occurs with acidic wash water systems. No further washing of nitroglycerine is necessary after direct treatment with sodium carbonate solution. Tank (*3*) is supplied with sodium carbonate solution through an automatic outlet valve coupled with a pH-meter. To neutralize 100 kg of nitroglycerine

ca. 7 kg anhydrous sodium carbonate is required (i.e. 52 l. of 12% solution). Each washing tank contains *ca.* 160 kg of emulsion.

A sample of the washed nitroglycerine is subjected to a heat-test. After removing sodium carbonate to max. 0.04%, nitroglycerine should give a positive test for 20 min at 80°C.

After stabilizing in the washing tanks the emulsion flows to another separator where the nitroglycerine is removed and sent for storage prior to incorporation. There is no final separator in the most recent Biazzi plants [44, 46]. The stabilized nitroglycerine is emulsified with warm water in (*5*) and flows to a low level storage tank.

The flow-sheet for the remote control of the nitroglycerine storage, transport and weighing installation is given in Fig. 49.

Stabilized nitroglycerine in the form of an aqueous emulsion flows into storage tank (*1*). If every batch of nitroglycerine is subjected to heat-test two storage tanks should be provided.

Water separated from the emulsion flows over to tank (*2*). The small quantity of nitroglycerine collected at the bottom can be sent back to (*1*) through the water pump (*3*) or drained through valve (*4*). If the nitroglycerine level is too high or too low a signal is given in the control room, that automatically sets in motion a number of injectors (*5*). They transport nitroglycerine from (*1*) to the weighing house and settling tank (*6*) until the level in the tank becomes satisfactory. The separated water flows to tank (*7*) and nitroglycerine collected at the bottom can be sent back through the water pump (*8*) or drained through valve (*9*). Nitroglycerine, free from water, passes through a common salt filter (*10*). Here the last traces of water are removed and the nitroglycerine is weighed in tank (*11*) which is mounted on scale (*12*).

Automatic filling of the weighing tank (*11*) is effected by pneumatic remote control through valve (*12*) and micrometric valve (*13*). The valves close automatically when the desired weight is reached.

Nitroglycerine flows out to the mixing room. The quantity of nitroglycerine in the weighing house is *ca.* 150 kg. As a rule no workmen come into contact with nitroglycerine in either the storage or the weighing house.

The great advantage of the Schmid–Meissner and the Biazzi processes is the small amount of separated explosive present in the plant at any given time—up to 10% (and 4% respectively) of the output per hour—the remainder of the nitroglycerine in the system is in a safe emulsified form.

The largest nitroglycerine plant in the world has been in operation since 1956 by I.C.I. of Australia and New Zealand Ltd. at Deer Park, Victoria [47]. The Biazzi system is used there. The normal output from this unit is 4400 lbs per hour of nitroglycerine, and it can be raised to 6600 lb [46].

One of most up-to-date Biazzi plants which came into operation in 1956 is the plant run by the Nobel Division of I.C.I. at Ardeer, Great Britain [48]. It has a production capacity of about 2500 lbs/hr (1130 kg/hr). The installation com-

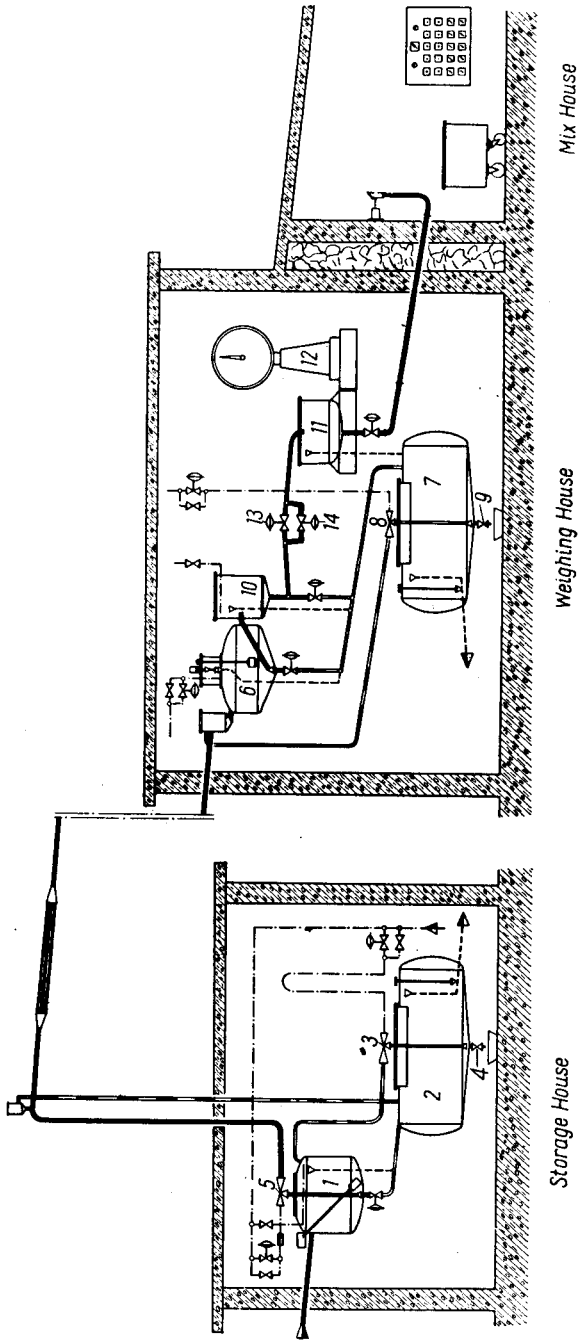

FIG. 49. Flow-sheet for a remote controlled nitroglycerine storage, transport and weighing installation according to Biazzi.

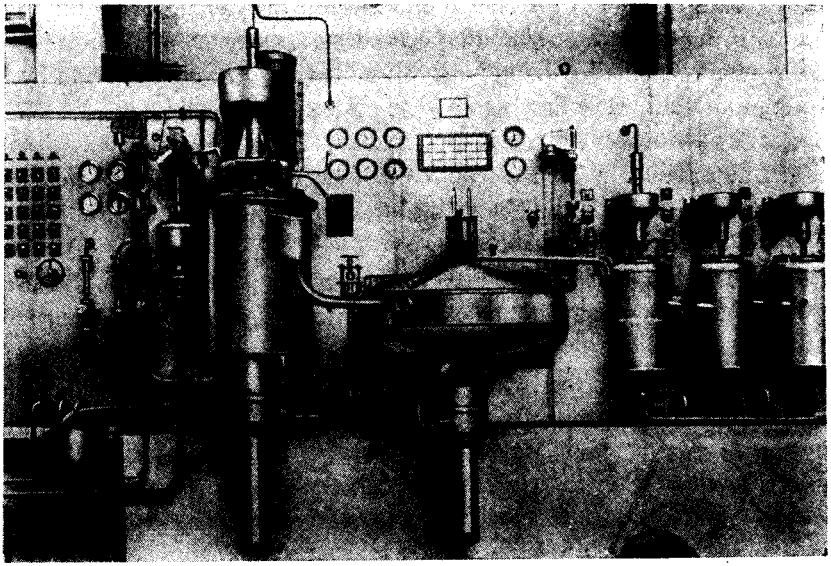

FIG. 50. Nitroglycerine manufacture — a general view of the nitrator, separator and washing equipment in a remote controlled Biazzi continuous plant (Ardeer Factory, Nobel Division, Imperial Chemical Industries Ltd., Great Britain, photograph of Vista of Glasgow, Glasgow, C 3).

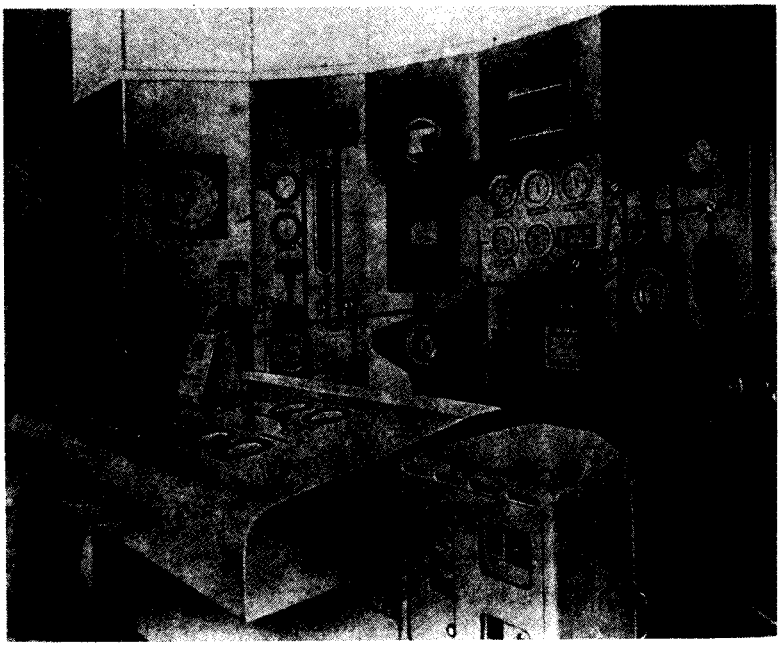

FIG. 51. Nitroglycerine manufacture — the remote control room of a Biazzi continuous plant (Ardeer Factory, Nobel Division, Imperial Chemical Industries Ltd., Great Britain, photograph of Vista of Glasgow, Glasgow, C 3).

VI. Automatic discharge of the contents of nitrator and separator into a drowning tank occurs, if the temperature in either exceeds the upper of safety limit.
VII. The contents of the drowning tank are subjected to forcible stirring by means of a strong jet of cold water flowing into the tank automatically.

The electrical control system is powered by means of 24-V batteries which are charged automatically from a rectified a.c. supply. All the control devices are located beyond the safety wall. The separator is monitored by a closed circuit television system.

Klassen and Humphrys [49] quote data comparing the main features of the Biazzi process as compared with batch nitration. The most recent data [50] are given in Table 18.

The Biazzi process has been applied to the nitration of other substances, to produce not only esters similar to nitroglycerine, but also for the preparation of such substances as PETN, cyclonite and TNT.

TABLE 18

	Nitrators producing 1200 kg nitroglycerine/hr	
	Biazzi	batch
Nitrator capacity, l.	125	305
Total cooling surface, m^2	10	23
Unit cooling surface, m^2/l.	0.08	0.0075
Time in nitrator, min	10	50
Heat transfer, kcal/m^2°C hr	800	365
Brine inlet temp., °C	−5	−25 to −20
Nitroglycerine in nitrator (at 4.7:1 acid ratio), kg	80	1590
	Raw materials and labour per 100 kg dry nitroglycerine	
Glycerine (and ethylene glycol 50:50), kg	42.2	42.2
Sulphuric acid (100%), kg	101	99
Nitric acid (100%), kg	104	99
Sodium carbonate, kg	6.0	1.7
Operating, labour-man-hours	0.04	0.18
Maintenance, labour-man-hours	0.01	0.08

N. A. B. INJECTOR NITRATION PROCESS (NILSSEN AND BRUNNBERG OR N. A. B. PROCESS)

This new method of manufacturing nitroglycerine developed by Nilssen and Brunnberg in 1950 at Nitroglycerin Aktiebolaget Gyttorp, Sweden [51] consists essentially in nitrating glycerine in an injector and separating nitroglycerine in a centrifuge. The flow of nitrating acid through an injector sucks in the correct amount of glycerine mixed with air. Nitroglycerine forms an emulsion with the spent acid.

After cooling, the emulsion flows into a centrifuge. Here nitroglycerine is separated from the spent acid and transferred to the washing house.

The main features of the N.A.B. process applied industrially since 1956 are as follows:

(1) **Mixed acid.** The nitrating acid is a conventional mixed acid, and spent acid is added in such a quantity that the HNO_3 content is 26.5–27.5% HNO_3 and the water content 9.5–10.0%. This water content is below the limit which may cause incomplete nitration. The ratio spent acid : mixed acid is 1.6–1.75.

(2) **Ratio acid : glycerine.** The flow of glycerine into the nitration injector is controlled by the flow of acid and this gives a high degree of safety for a reduction in the acid flow to less than the normal operating level results in a greater reduction of the glycerine flow.

The inlet pressure of the acid into the injector is 3.5 kg/cm^2 (50 p.s.i.) above atmospheric pressure.

(3) **Temperature.** A most important parameter characterizing nitration by injection is its high temperature, which lies within the limits 45–50°C. Small variations in temperature during normal operation are the result of small variations in the flow ratio of the reactants or in the initial temperature of the nitrating acid. This high temperature can be maintained for a short while owing to the particular conditions of the nitration, in which the heat of reaction is absorbed by a large mass of nitrating acid. Thus the temperature of the system is not dependent on the immediate removal of the heat of reaction as in other processes.

The glycerine or glycerine–glycol mixture (50:50) is pre-heated to 45–50°C before entering the injector.

The temperature of the mixed acid is 0°C.

The temperature increase during nitration, i.e. the difference between the nitrating temperature and the temperature of the incoming mixed acid, is a very good index of the ratio of glycerine to mixed acid. The exact value of the temperature rise depends on the HNO_3 content in the incoming mixed acid and on the spent acid, and the HNO_3 content of the latter depends (for a given concentration of mixed acid) on the ratio of glycerine to mixed acid.

In practice it has been found that an additional temperature rise of about 3°C corresponds to about a 1% decrease in the HNO_3 content of the spent acid and that a 1% higher HNO_3 content in the mixed acid gives a 1.7°C temperature rise for the HNO_3 content in the spent acid remaining constant. With the help of the diagram (Fig. 52) it can be seen what temperature increase will be obtained for a given mixed acid composition and for a given HNO_3 content in the spent acid.

If the temperature rises 4°C above the normal temperature, a warning signal is given and the flow of glycerine is reduced by the nitration operator. Should the amount of glycerine remain uncorrected despite the warning signal, and the temperature continues to rise, the electromagnet is de-energized at +54°C and the nitration process is stopped.

The nitroglycerine–acid emulsion enters a cooling system immediately after

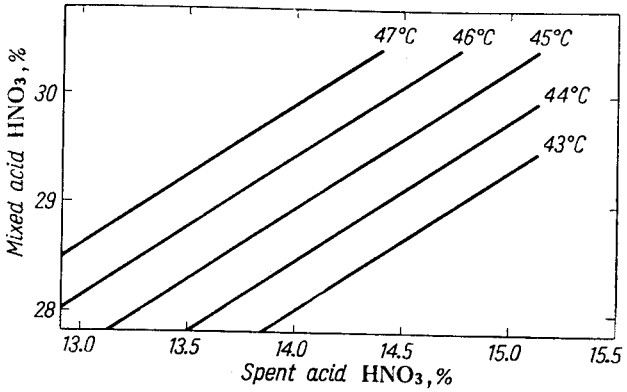

FIG. 52. Temperature diagram for injection nitration.

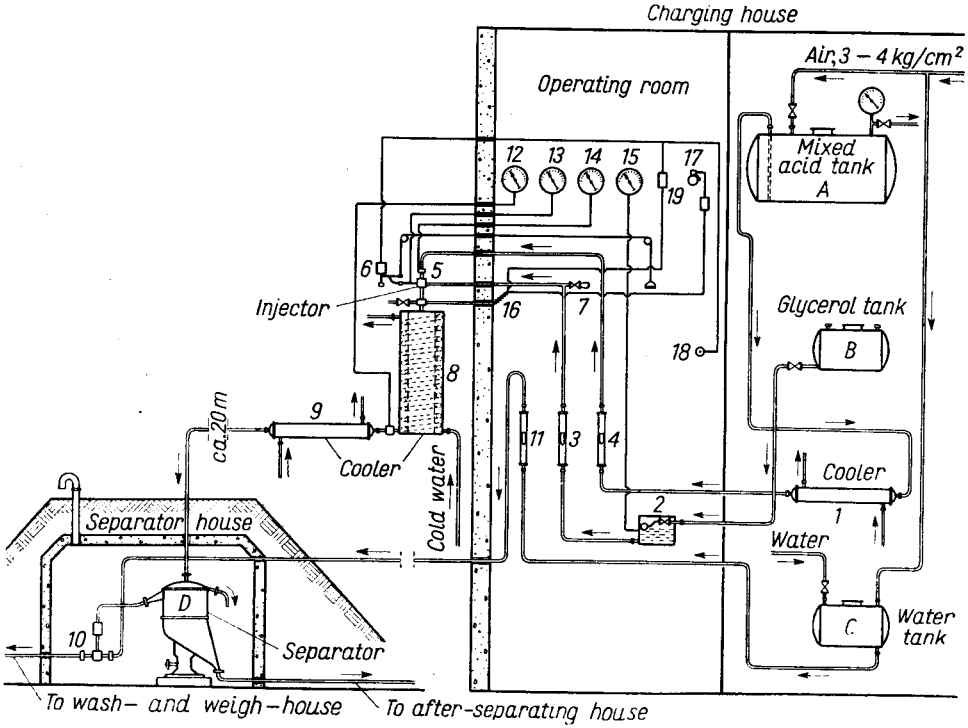

FIG. 53. Flow-sheet of injector nitration of glycerine and centrifugal separation of nitroglycerine at Gyttorp (Nitroglycerin Aktiebolaget Gyttorp, Sweden): *1* and *9*—tubular coolers (−12°C), *2*—glycerine suction tank with a constant level, *3*—glycerine rotameter, *4*—acid rotameter, *5*—injector-nitrator, *6*—electromagnet, *7*—needle valve for the air inlet to the injector, *8*—cold water cooler, *10*—injector to supply nitroglycerine-water emulsion, *11*—rotameter supplying water to *10,12,14,15*—thermometers, *13*—vacuum-meter, *16*—glass thermometer, *17*—alarm bell, *18*—current switch, *19*—relay to electromagnet *6*.

leaving the injector and the temperature of 45–50°C is maintained for only about half a second. During the next 80–90 sec the mixture is cooled to 15°C. In the following 30 sec the nitroglycerine is separated from the spent acid.

Cooling is achieved in two stages: the mixture is cooled to 25°C by ordinary water at 15°C and then it is cooled to +15°C by a cooling brine composed of a 30% solution of sodium nitrate at —12°C.

The flow sheet for injector-nitration and centrifugal separation is given in Fig.53 and the general view of the injector–nitrator in Figs. 54 and 55.

(4) **Separator** (Fig. 56). Another characteristic feature of the N.A.B. system is the continuous centrifugal separation of nitroglycerine from the spent acid. The centrifuge operates at 3200 r.p.m. For a unit with a capacity of 2500 l./hr the quantity of nitroglycerine in the separator bowl during operation is 3.5 kg. The separated acid nitroglycerine is emulsified immediately by the wash-jet to form a non-explosive mixture and is removed continuously from the separator house to the nitroglycerine wash-and-weigh house.

The spent acid from the separator contains a small amount of emulsified nitroglycerine. The portion which is to be used to prepare fresh mixed acid need not separated further, since when nitrating acid is added the emulsified oil redissolves and returns to the cycle.

The remainder of the spent acid is allowed to separate in the usual way and normally yields a maximum of 0.1% emulsified nitroglycerine. Instead of after-separation, water can of course be added to prevent separation.

(5) **Nitration.** To start the nitration, current from the switch (*18*) (Fig. 53) is applied to the electromagnet (*6*), which closes the air inlet to the injector. Mixed

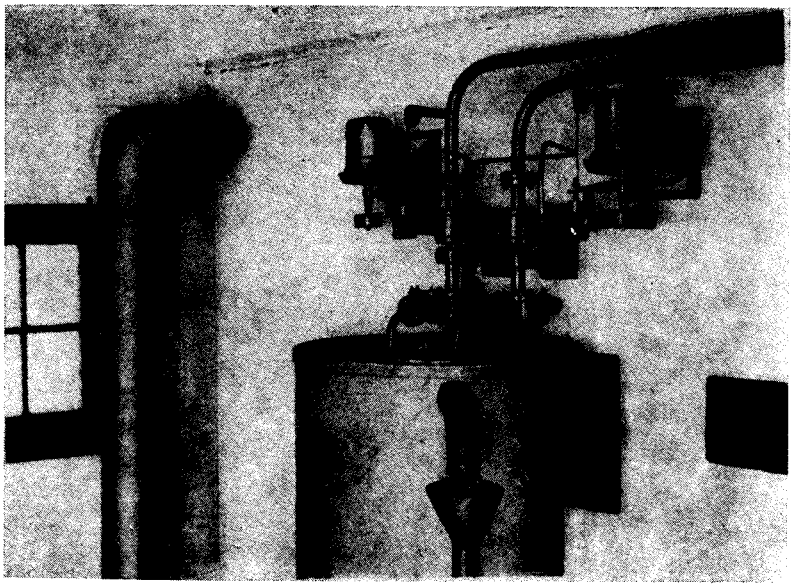

FIG. 54. Injector nitration apparatus at Gyttorp, general view (Nitroglycerine A. B. Gyttorp).

acid is admitted by opening the valve under the acid rotameter (*4*). The injector now comes into operation. The manometer (*13*) must show full vacuum. The needle valve (*7*) is then opened and the vacuum adjusted to *ca.* 300 mm Hg. The glycerine–glycol mixture is sucked in through the rotameter (*3*) to the injector from (*2*).

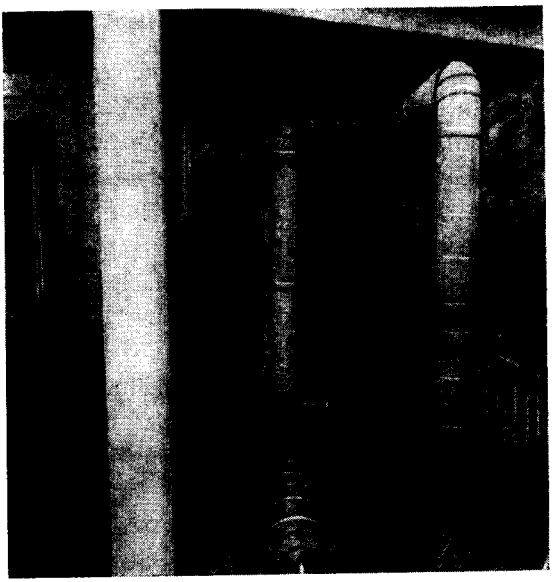

Fig. 55. Injector nitration apparatus at Gyttorp, side view (Nitroglycerine A. B. Gyttorp).

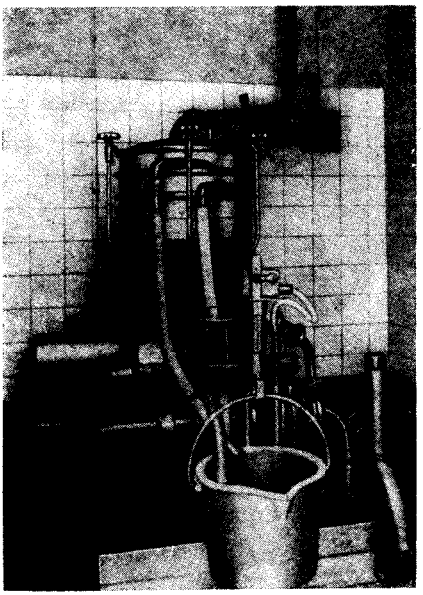

FIG. 56. Centrifugal separator of nitroglycerine at Gyttorp (Nitroglycerine A. B. Gyttorp).

The exact setting of the acid and glycerine rotameters is adjusted by means of the corresponding valves and the nitrating temperature is checked. It should be 40–45°C higher than the temperature of the incoming mixed acid.

Through the inspection glass nitroglycerine can be seen leaving the separator within about 2 min after nitration has begun.

To stop the process the circuit through the electromagnet (*6*) is broken at (*18*), so that air rushes into the injector and the glycerine in the pipe and in rotameter (*3*) runs back to (*2*). Mixed acid should be allowed to flow for 1 min in order to flush the pipes and cooling system. The separator is stopped about 10 min later and empties automatically.

The contents of the separator are collected in a special small separation vessel. The emulsified explosive oil is separated and delivered direct to the wash jet (*10*). After rinsing with separated spent acid, the separator is ready to be restarted.

A general view and a diagram of the operating room is given in Fig. 57 and 58 respectively.

Continuous washing of nitroglycerine is carried out in three wash columns: (*3*), (*6*) and (*9*), (Fig. 59).

Nitroglycerine Aktiebolaget Gyttorp quote the following figures which refer to the plant which has been in operation since 1956:

production: 500–650 kg nitroglycerine/hr
acid consumption: 2600–3400 kg/hr
glycerine consumption: 216–281 kg/hr
the yield of nitroglycerine–nitroglycol mixture is 231–232.5 kg of explosive oil, i.e. 93.9–94.5% of theoretical

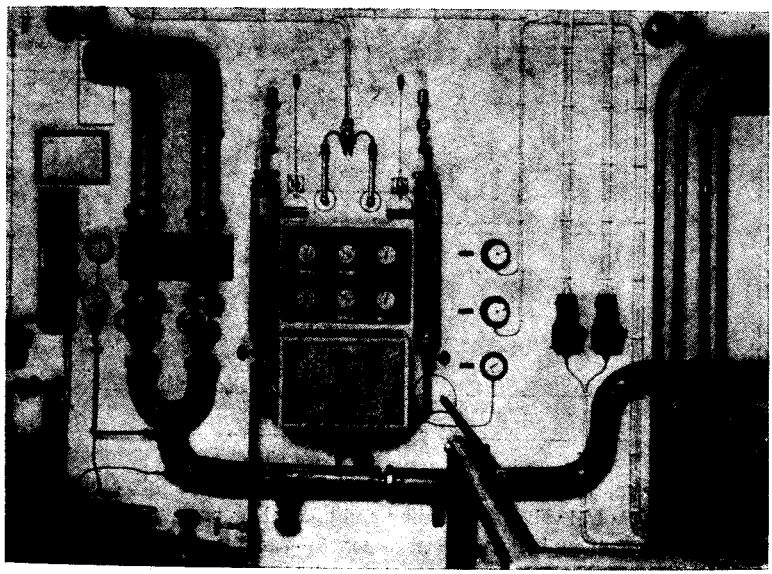

FIG. 57. Operating room, general view (Nitroglycerine A. B. Gyttorp).

brine (30% $NaNO_3$) consumption (Fig. 53):
cooler (*1*): *ca.* 75 l./min
cooler (*9*): *ca.* 100 l./min
water consumption cooler (*8*): 80–100 l./min
compressed air at 4 kg/cm² consumption: 1 m³/min

SEMI-CONTINUOUS PROCESSES

The invention of continuous methods of nitration of glycerine stimulated the improvement of the old batch processes by transformation into semi-continuous ones. One such methods was designed by Jarek [52] and is in use in Poland (Fig. 60).

The batch nitrator (*1*) is connected with a separator (*2*) and the drowning tank (*3*). The displacing acid tank (*4*) can produce a flow of nitroglycerine from the separator through the pipe (*6*) to the wash columns (*7*), (*9*) and (*11*). These columns

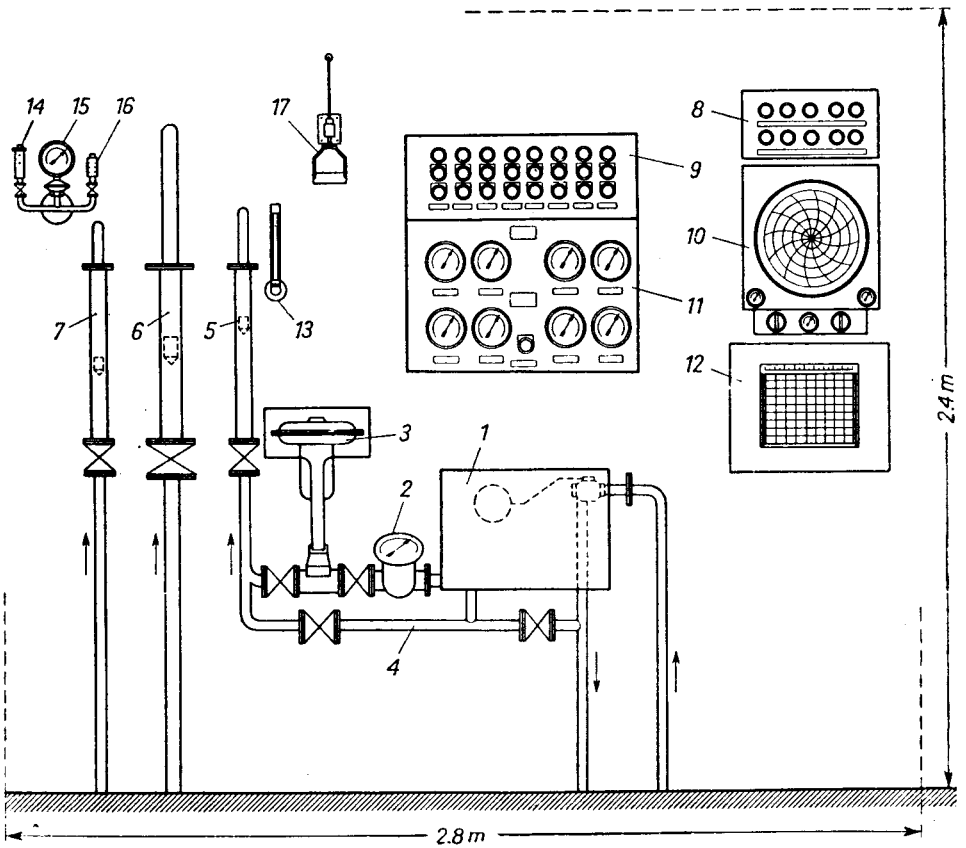

FIG. 58. Operating room, diagram (Nitroglycerine A. B. Gyttorp): *1*—glycerol vessel, *2*—glycerol meter, *3*—temperature control valve, *4*—draining and manual by pass, *5*—flow indicator glycerine, *6*—flow indicator acid, *7*—flow indicator wash water, *8*—signal lamps, *9*—switch board, *10*—temperature recorder controller, *11*—instrument board, *12*—temperature recorder, *13*—nitration thermometer, *14*—vacuum valve, *15*—vacuum gauge, *16*—air filter, *17*—emergency nitrating stopper.

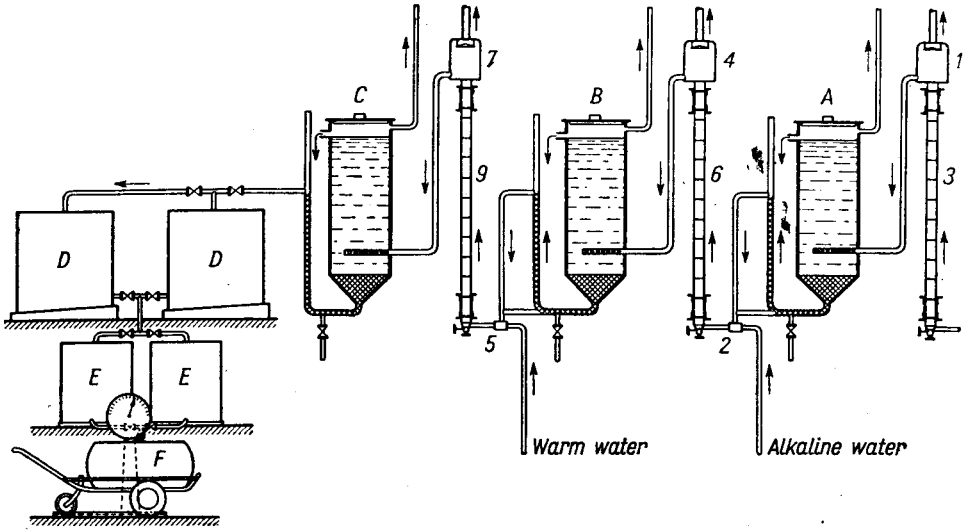

FIG. 59. Flow-sheet of washing nitroglycerine at Gyttorp: *A*—separator of acid wash-water, *B*—separator of alkaline wash-water, *C*—separator of warm wash-water, *D*—storage tanks, with wash-equipment, *E*—storage tanks with refrigerating coils, *F*—nitroglycerine waggon on a balance, *1*, *4*, *7*—air separators, *2*, *5*—injectors, *3*, *6*, *9*—wash-columns.

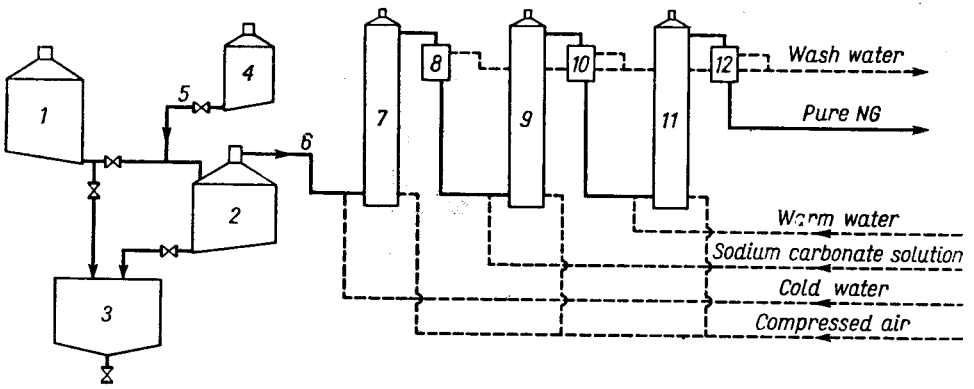

FIG. 60. Semi-continuous method of manufacture of nitroglycerine according to Jarek [52].

are connected with the separators (*8*), (*10*) and (*12*) respectively. The columns (*7*), (*9*) and (*11*) are fed with cold water, aqueous sodium carbonate solution and warm water respectively. The contents of the columns are agitated by means of compressed air fed to the bottom of the columns. Washed nitroglycerine flows from the bottom of the separators (*8*) and (*10*) to the columns (*9*) and (*11*) respectively. Nitroglycerine leaving the separator (*12*) is ready for use.

The method uses a batch nitrator but the separator (*2*) and the wash-columns run continuously.

GENERAL SAFETY RULES

The earliest plants for nitroglycerine manufacture were installed in buildings of very light construction made of planks and surrounded by a high mound of earth (Fig. 61).

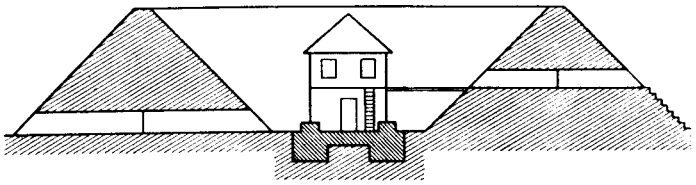

FIG. 61. Light building for manufacture of nitroglycerine with direct access to the lower and upper storeys.

Explosion of nitroglycerine is always violent and produces a large number of fragments partially retained by the safety mound. However, buildings of such light construction were unable to withstand the blast produced by an explosion in the neighbourhood. Another disadvantage was that in the event of explosion, not all the splinters were caught by the protective ramparts, and those that were projected beyond could initiate explosion in neighbouring parts of the plant.

Later, during World War I and since then, massive underground buildings made of concrete have become customary. Formerly this type of construction was used only for storage buildings. The underground buildings are semicylindrical in design and are completely buried except for the end intended for entrance and exit (Figs. 62 and 63).

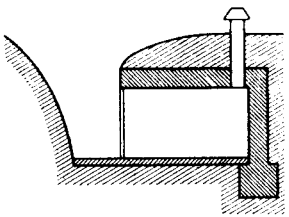

FIG. 62. Heavy underground building for manufacture of nitroglycerine.

If an explosion occurs the building is destroyed. However, owing to its robust construction no fragments are projected. Further the danger that the detonation might be transmitted from one building to another is reduced to a minimum. Towards the end of World War I 360 kg of nitroglycerine exploded in a German factory in the Rhineland but owing to its massive underground construction effects of the explosion were limited to the building concerned. Being situated in hollows, the buildings are fairly well earth-protected and danger of explosion by lightning is reduced to the minimum. Some disadvantage arises from the limited space which precludes certain changes or repairs, and from the high cost of the exhaust system.

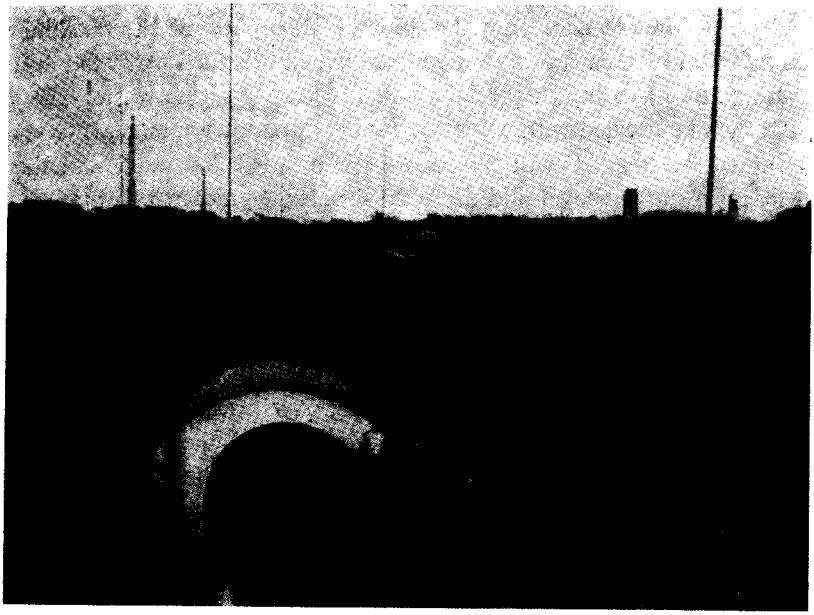

FIG. 63. General view of a heavy underground building.

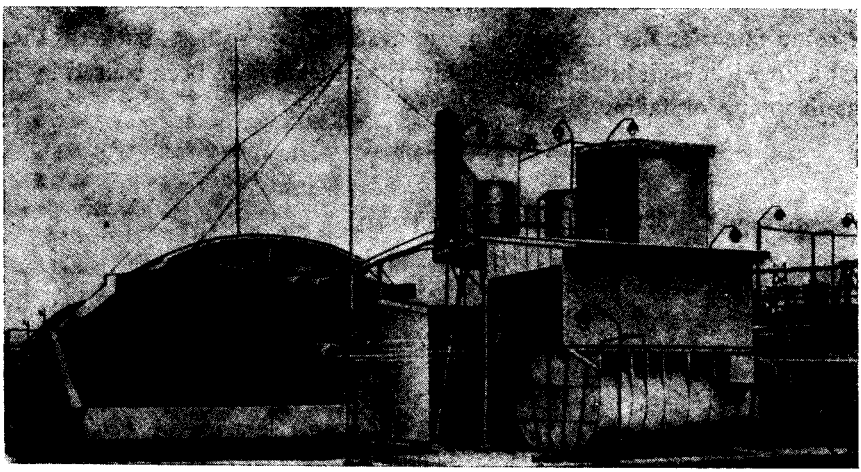

FIG. 64. Nitration Biazzi system building surrounded by earth mound with service tanks in centre and right foreground. The nitration building is protected by lightning arrestors [47]. (I.C.I. of Australia and New Zealand Ltd. at Deer Park, Victoria).

There is now a tendency to revert from underground buildings to less expensive lightly constructed surface ones, as for example the buildings for the modern Biazzi plant shown in Fig. 64.

The floor inside each building should be lined with sheet-lead, turned up at the edges close to the walls and door in order to form a border about 10 cm high, intended to contain any nitroglycerine that may be spilt.

Nitroglycerine that escapes onto the floor or onto parts of the machinery, etc. should be removed by means of a sponge from which it is then extracted and rinsed under a stream of water into a special vessel for nitroglycerine waste. The spillage area should then be washed with water, by means of another sponge. If acid escapes the area should be covered with siliceous earth or with fine sand, and the whole removed by means of a shovel and drowned in a large amount of water. A copper or aluminium shovel is necessary in case nitroglycerine is present in the acid.

All leaden apparatus should be cleaned and washed inside at least once a week to remove "lead slime". In all departments scrupulous cleanliness should be observed.

An old safety precaution required all work to stop in the nitroglycerine and dynamite factory during a thunderstorm passing over head. In the nitrating house no fresh charge could be started. All the men were to leave the building except those in charge of nitration and separation. Nowadays since the design of lightning-conductors has considerably improved, this regulation is not so necessary.

Every building must have a notice board at the entrance showing the maximum number of workman that may be in it at one time. Usually this number should not exceed two.

The maximum quantity of explosives in the building should also be limited and indicated.

In some factories the number of loose articles (e.g. bottles, buckets, thermometers) allowed in each house is also limited; accidents have been caused by heavy objects dropping or falling.

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CHAPTER IV

OTHER GLYCERINE ESTERS

THE most important drawbacks in the use of nitroglycerine are the danger of manufacturing and handling the material and its comparatively high freezing point. The danger of production has been partially overcome by improvements in manufacturing process and by strict observation of safety rules elaborated on the basis of many years' experience.

Much scientific effort has been devoted to the problem of how to lower the freezing point of nitroglycerine. This is very important from the practical point of view. If the nitroglycerine present in dynamite or in smokeless powder in the form of a gel is frozen, it separates in the form of an oil on melting. This seldom happens in the case of nitroglycerine powder, owing to its relatively low content of nitroglycerine, but the phenomenon is very frequent with dynamites. Handling dynamite from which oily nitroglycerine has partially separated is very dangerous because of the high sensitiveness of the oil to mechanical stimuli.

The problem of lowering the freezing point of nitroglycerine has been solved in many ways. Most of these methods are now of historical interest only, since they involved the use of substances which either weakened the explosive power of the nitroglycerine significantly or increased the price of product appreciably.

The first experiments on lowering the freezing point of nitroglycerine were undertaken by Rudberg [1] who blended nitroglycerine with nitrobenzene. Nobel [2] suggested admixing methyl and ethyl nitrate, nitrobenzene and glyceryl acetates. Methyl or ethyl nitrates certainly achieved the desired aim but owing to their high volatility, their use was of no practical value. Addition of the other substances mentioned reduced the explosive effect of the product.

The first effective work was carried out by Wohl [3], who proposed polymerizing the glycerine prior to nitration. At first the method was not widely used owing to various technical difficulties but eventually it found an application many years later (see p. 138). A Polish chemist, Antoni Mikołajczak (A. Mikolajczak) [4] is credited with being the inventor of the so-called low-freezing dynamites. In 1904 he obtained a patent for the production of glycerol dinitrate (so-called dinitroglycerine) and suggested adding this to nitroglycerine with a view to lowering the freezing point. Dinitroglycerine is a cheap substance and for several years Mikołajczak's invention was widely used. It also opened the way for further investi-

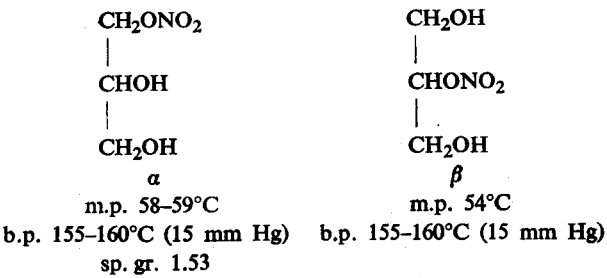
gations. In later patents of various authors the substances proposed for lowering the freezing point of nitroglycerine are glycerine derivatives, each molecule of which contains two nitrate groups, the third hydroxy group being esterified by another acid or being converted to an ether. Substances of this type include the so-called dinitrochlorohydrin, formyldinitroglycerine, acetyldinitroglycerine and tetranitrodiglycerine. Compounds containing one nitrate group, such as the so-called mononitroglycerine, nitrodichlorohydrin and nitroglyceride have found limited application.

The first theoretical basis for calculating the decrease of freezing point according to van't Hoff law as applied to nitric esters was given by Nauckhoff [5].

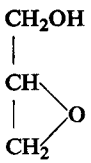
As progress was made in application of synthetic methods in the chemical industry, ethylene glycol obtained from ethylene became available and large scale manufacture of glycol dinitrate for blending with nitroglycerine in low-freezing dynamites began. Diethylene glycol also became a commercial product and yielded dinitrate used as an ingredient of smokeless ("double base") powders.

GLYCEROL MONONITRATE

Glycerol mononitrate (or "mononitroglycerine") exists in two isomeric forms, α and β:



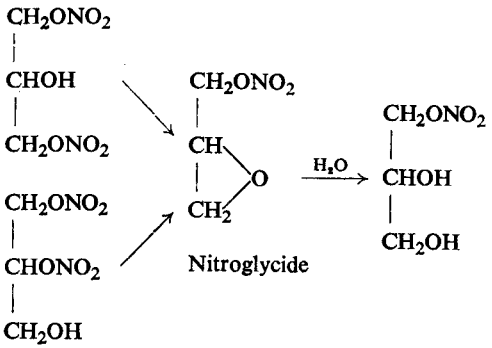
The pure α-isomer was first obtained by Hanriot [6] by nitrating glycide:



The properties of mononitroglycerine were investigated by Will *et al.* [7] and Naoúm [8].

Mononitroglycerine, mainly as the α-isomer, is a by-product accompanying dinitroglycerine produced by Mikołajczak's method [4]. Naoúm's method of separating of mononitroglycerines consists in making use of their appreciable solubility in water and relatively low solubility in ether, in which they differ from dinitroglycerines which are barely soluble in water but dissolve fairly well in ether. Thus, in order to isolate mononitroglycerines an aqueous solution of crude dinitroglycerine is prepared, and the dinitrates are extracted with ether. Mononitrates remain in the aqueous solution, from which water is removed by evaporating under reduced pressure to leave the mononitrates.

Pure α-mononitrate can be obtained by converting dinitroglycerine into "nitroglycide" which in the presence of hot water is hydrolysed to form the mononitrate. Afterwards water is removed under reduced pressure:



Both the free hydroxyl groups readily undergo esterification. By chemical reaction with benzoyl chloride, dibenzoates are obtained, namely:

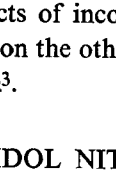
α-nitrate forms a dibenzoate of m.p. 68–69°C
β-nitrate forms a dibenzoate of m.p. 52°C

A characteristic addition product is formed by the α-nitrate with calcium nitrate (m.p. 117°C). Its composition is: $[C_3H_5(OH_2)(ONO_2)]_4.Ca(NO_3)_2$. The product is purified by crystallization in alcohol. β-Nitrate does not form such a compound.

Glyceryl mononitrates are stable substances which do not undergo decomposition when heated to a moderate temperature. In a sealed tube they decompose explosively at a temperature of about 170°C.

Mononitroglycerines are weak explosives. In consequence of a distinctively negative oxygen balance, only 434 kcal/kg are evolved on explosive decomposition (water in the form of vapour). Their sensitiveness to impact is extremely low. Indeed they are virtually insensitive. Their liability to detonate depends on their physical state. According to Naoúm the lead block expansion produced by liquid mononitroglycerine is 75 cm^3 only and products of incomplete decomposition, e.g. acrolein, are evolved. The crystalline product, on the other hand, detonates readily to produce an expansion amounting to 245 cm^3.

GLYCIDOL NITRATE

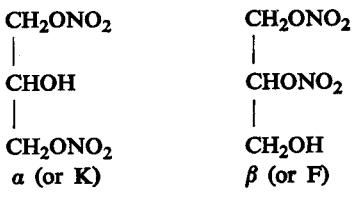


Glycidol nitrate ("nitroglycide") decomposes if boiled under normal pressure at a temperature of 174–175°C. Under a pressure of 20 mm Hg boiling takes place at 94°C. The specific gravity is 1.332 at 20°C.

As is stated above, glycidol nitrate is produced by hydrolysis of both isomeric glycerol dinitrates (Naoúm, 1907) [8]. According to Naoúm hydrolysis of the dinitrates is carried out by means of a 30% solution of KOH at room temperature. After a time the oily glycidol nitrate is precipitated with a yield of 95%. The oil is separated, washed with water and dried in desiccator. Nitroglycide dissolves slightly in cold water (5 g in 100 ml of water at 20°C). When boiled in water it yields α-glyceryl nitrate. Nitroglycide readily dissolves collodion cotton. Its explosive properties are well established. The heat of explosion is 824 kcal/kg. It detonates readily on impact (2 kg from 10–20 cm), and it explodes on heating to a temperature of 195 to 200°C. In a lead block with water tamping it produces an expansion of 430 cm^3.

GLYCEROL DINITRATE ("DINITROGLYCERINE")

Two isomeric glycerol dinitrates (dinitroglycerines) are known.

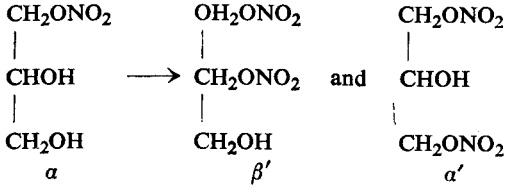


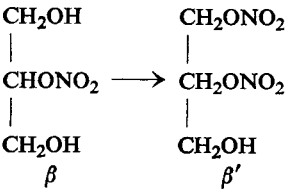
According to Will *et al.* [7] and Naoúm [8] the commercial product containing both isomers has a specific gravity of 1.47 at 15°C. On cooling it freezes at a temperature of —40°C. Under a pressure of 15 mm Hg it distils at 146°C almost without decomposition. It dissolves in water up to 8.6% at 20°C [25]. The product readily dissolves in most of organic solvents. It is insoluble in carbon tetrachloride and petrol. Being hygroscopic it picks up 10% of water at room temperature. It readily dissolves collodion cotton. Dinitroglycerine is nearly twice as volatile as nitroglycerine. Its physiological activity resembles that of nitroglycerine. The viscosity of dinitroglycerine is approximately twice as high as that of nitroglycerine due to intermolecular hydrogen bonds between the hydroxyl groups.

The isomers of dinitroglycerine have been separated by Will, Haanen and Stöhrer [7], utilizing the capacity of the α-isomer to form a crystalline hydrate. Thus by cooling dinitroglycerine with a 3.2% water content, crystallization of the hydrate occurs, whilst the β-isomer hydrate remains in solution. The α-isomer hydrate, melting at 26°C, has the formula: $[C_3H_5(OH)(ONO_2)_2]_3.H_2O$. It dissolves readily in water and benzene. At a temperature of 40°C both hydrates lose their combined water.

According to Will *et al.* the chemical structure of the isomers can be demonstrated as follows. By introducing one more nitro group to the α-mononitrate, two isomeric dinitrates — a symmetric α' and an asymmetric β' — are formed.

By nitrating the β-mononitrate, on the other hand, only one product, i.e. the asymmetric dinitrate β', can result.





As mentioned above, dinitroglycerine is hydrolysed in the cold in the presence of a concentrated potassium hydroxide solution to form nitroglycide.

Dinitroglycerine is more resistant to heating than nitroglycerine: it begins to show signs of decomposition after 14 days' heating at a temperature of 75°C. On heating to 150°C it evolves brown fumes of oxides of nitrogen, on heating above 170°C it undergoes explosive decomposition, the latter being the more violent the larger the amount of the substance heated.

EXPLOSIVE PROPERTIES

According to Naoúm [8] the explosive decomposition of dinitroglycerine can be expressed by the equation:

$$C_3H_5(OH)(ONO_2)_2 \longrightarrow 2CO_2 + CO + 2H_2O + N_2 + H_2 + 1201 \text{ kcal/kg}$$

The large thermal effect entitles this substance to be regarded as a very powerful explosive. Its sensitiveness to shock is barely less than that of nitroglycerine, as it explodes under the impact of a 2 kg weight dropped from a height of 7–10 c ı.

The crystalline α-dinitrate hydrate explodes under the impact of a weight dropped from a height of 90–100 cm; for explosion of the liquid β-isomer a drop of only 30–40 cm is required.

In the lead block with water tamping, dinitroglycerine gives an expansion of 500 cm^3. Under these conditions nitroglycerine causes an expansion of 600 cm^3. A 92% blasting gelatine made from dinitroglycerine produces an expansion of 440 cm^3, whereas the same gelatine made of pure nitroglycerine produces an expansion of 585 cm^3. Considering these experiments and the heat of detonation, the explosive strength of dinitroglycerine seems to amount about 80% of that of nitroglycerine.

To bring about complete detonation, as with liquid nitroglycerine, a rather

powerful initiator is necessary. Thus the expansion in the lead block test, using a No. 1 detonator amounts to 290 cm^3, whereas that produced by a No. 8 detonator is 500 cm^3 (with water tamping).

The detonation rate of 92% dinitroglycerine blasting gelatine is 3300 m/sec, according to Blochmann [9] the corresponding value for nitroglycerine being 7000 m/sec.

For a 75% Kieselguhr dynamite made from dinitroglycerine the rate of detonation is 4300 m/sec (with nitroglycerine it is 6800 m/sec).

According to Blochmann transmission of detonation from a 100 g charge of blasting gelatine made from dinitroglycerine is 5 cm, whereas for nitroglycerine gelatine it is 25 cm.

MANUFACTURE OF DINITROGLYCERINE

The sole commercially important method of manufacturing dinitroglycerine is that developed by Mikołajczak [4]. Glycerine is dissolved at a temperature of 15–20°C in 3–4 parts of nitric acid as free as possible from oxides of nitrogen. In order to achieve complete nitration the solution is allowed to stand for 2–6 hr. Then it is diluted with water in the proportion of 1 part of water and ice to 1 part of acid, and finally neutralized with calcium carbonate thus forming a concentrated calcium nitrate solution (1.51 g/ml). Being insoluble in this solution, which is of high density, dinitroglycerine rises to the surface to form an oily layer. This oil is separated and washed by means of a concentrated sodium chloride solution containing sodium carbonate or ammonia. Sodium chloride is added to lower the solubility of the dinitroglycerine, so that washing can be carried out even at 40–50°C with negligeable loss of the product. (8 parts of dinitroglycerine dissolve in 100 parts of water at 20°C whereas only about 2 parts dissolve in 100 parts of a 30% solution of sodium chloride). Finally the dinitroglycerine is rinsed with a solution of sodium chloride. In order to minimize the loss of dinitroglycerine, the same solution of sodium chloride is used several times.

If nitrous and nitric oxides are present in the nitric acid, products of oxidation may contaminate the main product. Such dinitroglycerine should be washed with special care. The product is dried by passing a stream of warm air through it.

The calcium nitrate solution is treated with a calculated quantity of ammonium sulphate to precipitate calcium sulphate and ammonium nitrate is recovered from the resulting solution by evaporation, for use in the manufacture of explosives.

The raw materials consumption in the production of 100 kg of dinitroglycerine is as follows:

glycerine	71.4 kg
nitric acid	250 kg
ice	75 g
calcium carbonate	125 kg
ammonium sulphate	165 kg
ammonia	1.5 kg

The following by-products are obtained:

ammonium nitrate	200 kg
calcium sulphate	165 kg

The consumption of raw materials is such that the price of dinitroglycerine is higher than that of nitroglycerine.

The Mikołajczak process is usually safer than nitroglycerine manufacture. It is necessary, however, to maintain a low nitrating temperature and to use acid free from oxides of nitrogen which favour oxidation reactions. Local overheating should be carefully avoided, because dilute acid is specially prone to produce oxidation processes.

According to du Pont Company [10], ammonia can be used for the neutralization of the dilute solution of dinitroglycerine in nitric acid, thus producing a solution of ammonium nitrate which is recoverable.

Pütz [11] obtained a patent for the preparation of dinitroglycerine relatively free from the trinitrate by dissolving 1 part of glycerine in 3.3 parts of nitric acid (sp. gr. 1.5) below 15°C. The solution was diluted with 1 part of water and neutralized with calcium carbonate. The product was separated as an oil and a small quantity was extracted with ether from the aqueous solution.

Dinitroglycerine was also obtained from nitroglycerine by denitrating it with sulphuric acid [12, 25]. The denitration occurs simply by dissolving nitroglycerine in conc. sulphuric acid without cooling. The solution is dissolved in water and the dinitroglycerine extracted with ether.

Commercial dinitroglycerine contains a certain amount of glycerol mononitrate and trinitrate. In dynamites dinitroglycerine is blended with nitroglycerine, hence in a number of patents it has been proposed to nitrate glycerine in conditions which enable a low freezing mixture of nitroglycerine and dinitroglycerine to be obtained in one operation. In principle a higher yield is obtained when more acid is used for the nitration. For the nitration of 100 parts by weight of glycerine, Naoúm [8] obtained the following results which are tabulated below (Table 19).

TABLE 19

THE RESULTS OF NITRATING 100 PARTS BY WEIGHT OF GLYCERINE (AFTER NAOÚM)

Amount of 95% HNO_3 used to nitrate, in parts by weight	Yield of esters, parts by weight			Percentage ratio	
	total	nitro-glycerine	dinitro-glycerine	nitro-glycerine	dinitro-glycerine
250	77.3	6.8	70.5	9	91
350	127.5	20.5	107.0	16	84
450	175.6	44.8	130.8	26	74
500	191.0	51.0	140	27	73

A few papers [7, 25] and patents [13] suggest the preparation of dinitroglycerine by nitrating with a dilute mixed acid (e.g. containing 9% water), followed by dilution

of the whole with water to separate dinitroglycerine. This method, however, is uneconomic.

Other patents [4, 11] recommend manufacturing blends of dinitroglycerine and nitroglycerine in any ratio by nitrating glycerine with mixed acid containing less sulphuric acid than usual, for example, a mixture containing

HNO_3	60%
H_2SO_4	30%
H_2O	10%

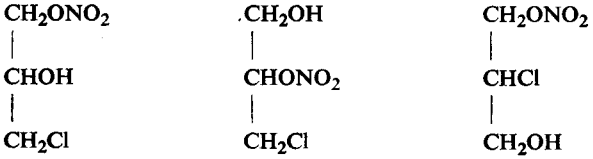
yields an oily product, the dinitrate to trinitrate ratio of which is *ca.* 70:30. The separation of the oil is followed by dilution of the spent acid with water to precipitate a further quantity of oil containing a higher proportion of dinitroglycerine, e.g. *ca.* 90:10.

MIXED GLYCERINE ESTERS

CHLOROHYDRIN NITRATES

Mononitrochlorohydrin

Mononitrochlorohydrin is a chlorohydrin mononitrate, existing in the three isomeric forms shown below:



All are obtained by nitrating chlorohydrin with not overmuch concentrated nitric acid, e.g. with a threefold excess of 80% acid. They can also accompany dinitrochlorohydrin as impurities. Owing to the presence of a hydroxy group they are moderately soluble in water. In the warm they dissolve collodion cotton. Mononitrochlorohydrin has weak, but distinct explosive properties; it can be made to detonate by a strong initiator though it is not exploded by impact.

Dinitrochlorohydrin

The most important of the chlorohydrin nitrates are the chlorohydrin dinitrates ("dinitrochlorohydrins"), existing in two isomeric forms:

Dinitrochlorohydrin was first obtained by Henry [14] and Volney (15] who was the first to call attention to its explosive properties. It was used in blends with nitroglycerine for the manufacture of non-freezing dynamites [16, 17] as early as in 1904 and since then it has been rapidly adopted for this purpose in some countries, owing to its relative cheapness and simplicity of manufacture. The commercial product is a mixture of both isomers, the α-isomer predominating. Cooling to a temperature of —20°C usually fails to convert the substance into a solid since it is liable to supercooling. The specific gravity is 1.541 at 15°C. At 190°C commercial dinitrochlorohydrin boils and rapid decomposition occurs, whereas "boiling" under reduced pressure at 10 mm Hg occurs at 117.5°C with little decomposition. Dinitrochlorohydrin is more volatile than nitroglycerine. Naoúm reported that the loss of weight from a vessel of 50 mm diameter after standing for a day at 75°C was 3.1%, for dinitrochlorohydrin and 0.35% for nitroglycerine. It is non hygroscopic and dissolves in water only to small extent (about 2.3 g in 1 l. of water at 15°C). It dissolves with ease in most organic solvents, except carbon disulphide and petrol. Dinitrochlorohydrin mixes with nitroglycerine at any proportion, such mixtures having a very low freezing point. A blend of 75% nitroglycerine with 25% dinitrochlorohydrin can be considered practically non-freezing.

Collodion cotton is soluble with difficulty in pure dinitrochlorohydrin. Dissolution takes place more rapidly in the warm, but on cooling the dinitrochlorohydrin separates again from the sol. In blends of dinitrochlorohydrin with nitroglycerine nitrocellulose dissolves with great ease. Dinitrochlorohydrin is less viscous than nitroglycerine. According to Naoúm [8] its relative viscosity is 155, taking the viscosity of water as 100, as compared with 278 for the relative viscosity of nitroglycerine.

The chemical stability of dinitrochlorohydrin is higher than that of nitroglycerine. It withstands the Abel heat test at 72°C for 30 min. On heating at a temperature of 75°C, the first signs of decomposition and the development of acid fumes do not appear before 10–12 days. A small quantity of chlorohydrin dinitrate heated in a test tube undergoes decomposition with the evolution of oxides of nitrogen at temperature above 170°C. Complete decomposition takes place (without explosion at 180°C. Larger quantities of the substance decompose with a weak explosion, if heated rapidly to a temperature of about 190°C.

The explosive properties of dinitrochlorohydrin are as follows. The heat of explosion determined by Naoúm [8] in a calorimeter bomb (water in the liquid state, hydrogen chloride as hydrochloric acid) is 1140 kcal/kg. This value corresponds to a heat of explosion of 1000 kcal/kg when water and hydrogen chloride are assumed to be in the gaseous state in agreement with the equation given by Naoúm:

$$C_3H_5Cl(ONO_2)_2 \longrightarrow CO_2 + 2CO + 2H_2O + HCl + N_2 + 1000 \text{ kcal/kg}$$

Decomposition in accordance with the following equation is also possible:

$$C_3H_5Cl(ONO_2)_2 \longrightarrow 2CO_2 + CO + H_2O + H_2 + HCl + N_2 + 1050 \text{ kcal/kg}$$

Dinitrochlorohydrin can be ignited with difficulty to burn calmly without explosion. Chlorohydrin dinitrate placed in a can and thrown into a fire burns quietly, whereas in these circumstances nitroglycerine explodes. Dinitrochlorohydrin is less sensitive to shock than nitroglycerine or dinitroglycerine. According to Kast [18] in a drop test with a weight of 2 kg dinitroglycerine explodes on impact from a height of 10–20 cm (for nitroglycerine a height of 4 cm is sufficient to initiate explosion). The explosion of dinitrochlorohydrin caused by impact is appreciably weaker than that of nitroglycerine. Owing to its low sensitiveness to impact and the small risk of explosion on burning [19] in Germany chlorohydrin dinitrate was regarded as an explosive safe for transport by rail in containers of 25–200 kg.

Dinitrochlorohydrin produces the following expansion in the lead block (Naoúm) [8]:

with a No. 8 detonator and water tamping	475 cm^3
with a No. 1 detonator and water tamping	380 cm^3
blasting gelatine (made with 42% of dinitrochlorohydrin)	440 cm^3

The rate of detonation of dinitrochlorohydrin is lower than that of nitroglycerine, but no exact data have been reported.

The explosive strength of dinitrochlorohydrin is assumed to be about 80% that of nitroglycerine. As a component of mining explosives chlorohydrin dinitrate has the disadvantage of producing hydrogen chloride on explosion. It does not seem to be any more of practical use.

The raw material from which dinitrochlorohydrin is produced is chlorohydrin, made by treating glycerine with hydrochloric acid at a temperature of 100–120°C under pressure [20]. The substitution product is a mixture of α- and β-isomers. (The boiling point of α-chlorohydrin is 130°C at 18 mm Hg; that of β-chlorohydrin is 146°C at 18 mm Hg).

Chlorohydrin for the manufacture of dinitrochlorohydrin must be as pure as possible and should contain the minimum amount of water, HCl and polymerization products of glycerine, since the presence of these substances favours the formation of an emulsion during nitration and washing. Usually chlorohydrin was made in the explosives factory. After a single distillation the substance was transferred to the nitrating unit generally in admixture with glycerine.

Dinitrochlorohydrin is formed by nitrating monochlorohydrin with mixed acid in a manner analogous to the nitration of glycerine. Less heat is evolved than during the nitration of glycerine, and the operation can therefore be carried out more rapidly. Chlorohydrin is also less viscous than glycerine so that separation of the nitrated product is accomplished in a shorter time than in the corresponding process in nitroglycerine manufacture.

When 450 parts by weight of mixed acid composed of

40%	HNO_3
60%	H_2SO_4

are used to treat 100 parts of chlorohydrin at a temperature of 10–15°C, 161.5 parts of dinitrochlorohydrin (both isomers) are obtained, i.e. an 89% theoretical yield.

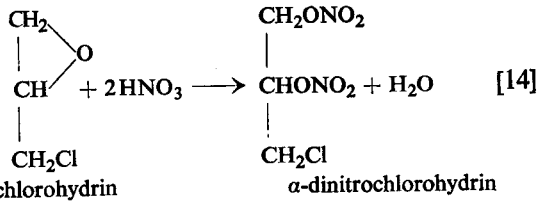
The composition of the spent acid is:

HNO_3	16.6%
H_2SO_4	75.0%
H_2O	7.4%

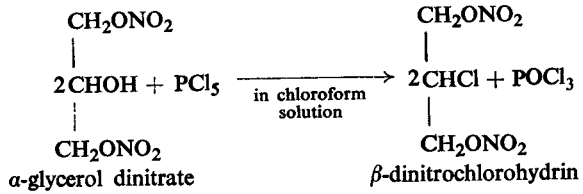
The solubility of dinitrochlorohydrin in the spent acid is negligible.

In practice, usually a mixture of chlorohydrin with 10–20% of glycerine is nitrated, to yield 165–175 parts of chlorohydrin dinitrates with nitroglycerine.

The pure isomers are obtained by the following chemical reactions:



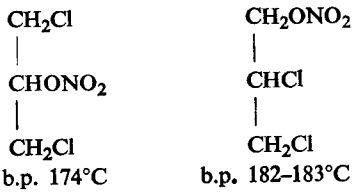
Epichlorohydrin — α-dinitrochlorohydrin [14]



α-glycerol dinitrate — β-dinitrochlorohydrin [8]

DICHLOROHYDRIN NITRATES

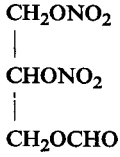
Two isomers of dichlorohydrin nitrate exist, also called "nitrodichlorohydrins" [14]:



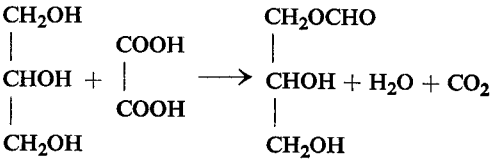
b.p. 174°C — b.p. 182–183°C

A mixture of these isomers has been suggested for addition to nitroglycerine for the production of low-freezing dynamites [21]. However, it possesses many properties undesirable for a component of explosives. It is more volatile than dinitrochlorohydrin, it is a poor solvent of collodion cotton and its explosive strength is insignificant. The heat of explosion developed by nitrodichlorohydrin is approximately 350 kcal/kg and the lead block expansion is 75 cm^3 including the effect produced by the initiator. For these reasons nitrodichlorohydrin has not found practical application. Nitrating dichlorohydrin by means of a water-free mixed acid is carried out with ease to produce a 94.5% yield (127.5 parts of nitrodichlorohydrin are obtained from 100 parts of dichlorohydrin).

FORMYLGLYCEROL DINITRATE



α-Formylglycerol dinitrate ("dinitroformylglycerine") is a strong explosive, its explosion producing about 1000 kcal/kg of heat. It is obtained as follows: 2 moles of glycerine are heated with 1 mole of anhydrous oxalic acid to a temperature of 140–150°C during a period of 20 hr to form monoformylglycerol:

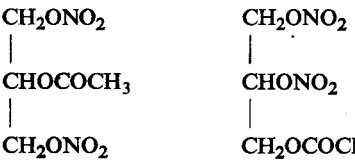


A proportion of the glycerine remains unchanged and the resulting product is a solution of formylglycerol in glycerine. This is nitrated by means of a mixed nitric and sulphuric acid to yield a mixture containing 70% of nitroglycerine and 30% of dinitroformylglycerol.

The explosion of this mixture which was proposed by Vender [22] as an additive to nitroglycerine in the manufacture low-freezing dynamites produces approximately 90% of the explosive power of nitroglycerine.

ACETYLGLYCEROL DINITRATE

Acetylglycerol dinitrate ("dinitroacetin", "nitroacetin") exists in two isomeric forms:



This is another explosive suggested by Vender [22] for lowering the freezing point of nitroglycerine.

The commercial product composed of both isomers does not freeze at —20°C. Its boiling point is 147°C under 15 mm Hg. The specific gravity is about 1.42 at 15°C. Commercial nitroacetin is more volatile than nitroglycerine but less so than dinitrochlorohydrin. It is insoluble in water. Lower and even higher nitrated cellulose is dissolved in it with ease. The substance is a little less stable than nitroglycerine, because it undergoes a distinct decomposition accompanied by the evolution of oxides of nitrogen after being kept for 24 hr at a temperature of 75°C. Heated in

a test tube it starts to decompose at 160°C. At 170–180°C decomposition proceeds violently. According to Naoúm [8] explosive decomposition is accompanied by the production of about 660 kcal/kg of heat.

Acetylglycerol dinitrate is almost insensitive to shock. Initiated with a No. 8 detonator it gives a lead block expansion of about 200 cm^3. A 92% blasting gelatine made from dinitroacetin produces an expansion of about 145 cm^3.

In comparison with dinitrochlorohydrin, dinitroacetin is more expensive but has the advantage that it does not evolve gases detrimental to health. In spite of this, the substance found only limited and transient application.

For blasting purposes mixtures in the proportion of 80 parts of nitroglycerine to 20 parts of dinitroacetin were usually used. This composition has an explosive strength of about 90% that of nitroglycerine. The manufacture of dinitroacetin, reported by Vender [22], consists in nitrating monoacetyl glycerol (monoacetin) by means of anhydrous mixed acid at a temperature below 25°C in the same kind of apparatus as that used for nitrating glycerine, the product being washed in the usual way. The yield is 159 parts by weight of dinitroacetin from 100 parts of monoacetin, i.e. 95% of theoretical.

POLYGLYCEROL ESTERS

As mentioned earlier the idea of nitrating glycerine polymerized by dehydration was suggested by Wohl [3]. He obtained a low-freezing blasting oil. However, this idea has not found an immediate practical application. One problem was the difficulty of feeding a nitrator with polyglycerine either dispersed as droplets or in the form of a thin stream owing to its very high viscosity. An even greater drawback was the tendency of polyglycerol nitrate to form emulsions not easy to separate and purify due to the presence of impurities.

Wohl proposed to polymerize glycerine by heating it with a small amount of sulphuric acid at a temperature between 130 and 160°C. Further investigations were reported by Will [23] who discovered that polymerization accompanied by the formation of water is most successful when glycerine plus a small quantity of sodium carbonate or sulphite (about 0.5%) is heated to a temperature approaching its boiling point. i.e. 290°C. The main product is diglycerol ether, more strictly 2,2′,3,3′-tetrahydroxydipropyl ether [*sym*-bis(2,3-dihydroxypropyl) ether], or the so called "diglycerine":

$$2C_3H_5(OH)_3 \longrightarrow CH_2OH—CHOH—CH_2—O—CH_2—CHOH—CH_2OH + H_2O$$

Triglycerine and polyglycerine are produced in inappreciable quatities (4–6%). The residual 30–40% is unchanged glycerine. The mixture can be nitrated directly and none of the difficulties accompanying the nitration of polyglycerol reported by Wohl occur. Diglycerine, the chief component of the mixture, starts to boil under a reduced pressure of 8 mm Hg at a temperature of 245–250°C. Its specific gravity is 1.33 and its viscosity is about 11 times greater than that of glycerine.

DIGLYCEROL TETRANITRATE

By nitrating "diglycerine" diglycerol tetranitrate, also called "tetranitrodiglycerine" or simply "nitrodiglycerine", is obtained:

$$CH_2ONO_2—CHONO_2—CH_2—O—CH_2—CHONO_2—CH_2ONO_2$$

Nitrodiglycerine is a liquid more viscous than nitroglycerine, which does not freeze even if subjected to the strongest cooling. It does not dissolve in water and is non-hygroscopic. Like nitroglycerine, it dissolves in the majority of organic solvents. Collodion cotton is only partially dissolved by it. The chemical stability of dinitroglycerine is not less than that of nitroglycerine.

The explosive properties of nitrodiglycerine are as follows. According to the work of Naoúm [8] and Will [7] nitrodiglycerine is capable of undergoing an explosive decomposition in accordance with the following equation:

$$C_6H_{10}N_4O_{13} \longrightarrow 2CO_2 + 4CO + 5H_2O + 2N_2 + 1330 \text{ kcal/kg}$$

Thus the substance is one of the strongest explosives known, and a composition made from 75% of nitroglycerine and 25% of nitrodiglycerine gives practically the same thermal effect as that caused by pure nitroglycerine.

In comparison with nitroglycerine, nitrodiglycerine has the advantage of being less sensitive to shock; it explodes on the impact of a 2 kg weight falling from a height of 8–10 cm.

The nitration of diglycerine to nitrodiglycerine is usually performed in the same way as the nitration of glycerine, certain differences being occasioned by the different properties of the substances. For the nitration of diglycerine slightly less mixed acid is needed than in the case of nitroglycerine. This is clear from the stoichiometric proportions and also follows from the fact that diglycerine is more prone to oxidation than glycerine and more sensitive to the action of an excess of nitrating acid. Owing to its high viscosity, diglycerine is heated up to 50–60°C before being introduced into the nitrator.

The separation of nitrodiglycerine is slower than that of nitroglycerine, mainly due to the high viscosity of nitrodiglycerine and to its tendency to form emulsions. The more impure the diglycerine, the easier is the formation of emulsions. After the separation of nitrodiglycerine, washing with a solution of common salt follows, the presence of which prevents emulsification. Moisture retained by the washed product is appreciably more difficult to remove than from nitroglycerine.

100 parts of diglycerine yield 168 parts of nitrodiglycerine, i.e. 81% of the theoretical yield. In practice the most commonly used method is the nitration of a mixture of 60–70% glycerine with diglycerine, from which a virtually non-freezing mixture of nitric esters is obtained [24].

Nitrodiglycerine is superior to dinitrochlorohydrin in low-freezing dynamites since it does not evolve hydrogen chloride among the explosion products. Also in favour of nitrodiglycerine is the fact that it does not dissolve in water. A further

advantage is the ease of preparation of mixtures of diglycerine and glycerine. On the other hand, however, the removal of impurities from such mixtures presents difficulty, and their presence leads to difficulties in manufacturing the nitric ester. The high viscosity of diglycerine and of the resulting nitration product is also a disadvantage in the manufacturing process.

For these reasons, nitrodiglycerine has not been adopted in practice in some countries e.g. in Germany, where dinitrochlorohydrin was for many years the most widely used raw material until it was replaced recently by nitroglycol. Nitrodiglycerine came into a broad use only in Great Britain in the years between 1920 and World War II.

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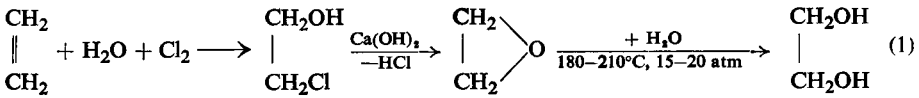
CHAPTER V

GLYCOL ESTERS

ETHYLENE GLYCOL ESTERS

THE first reference to the application of ethylene glycol dinitrate ("nitroglycol"), as a component of explosive mixtures was published by Claessen [1] as early as 1904 and Propach [2] in 1905. Subsequently in the years 1909–1914 [3] the original experiments were carried out aimed at decreasing the freezing temperature of nitroglycerine by adding nitroglycol. At that time the manufacture of glycol was based on the hydrolysis of dibromoethane. The method was very expensive and did not produce an economic yield, so glycol was not then manufactured on a commercial scale.

As a result of the acute shortage of glycerine that occurred in Germany during World War I a method was developed for manufacturing ethylene glycol by the hydrolysis of dichloroethane. However, this reaction produces a number of glycols of different chain length composed of various numbers of ethylene oxide units. Hence the method was superseded by another, which is still in use, consisting in the following chemical reactions:



(1)

In the presence of hypochlorous acid ethylene reacts to form ethylene chlorohydrin which, by means of calcium hydroxide in aqueous solution, is converted into ethylene oxide. The ethylene oxide is then hydrolysed with water to form glycol. In addition to ethylene glycol ("glycol") a certain amount of diethylene glycol ("diglycol") and triethylene glycol ("triglycol") are formed. On the average the percentage composition of the product is as follows:

glycol	87–89%
diglycol	9–11%
triglycol	2–3%

All these components are capable of being nitrated.

Glycol, diglycol and triglycol are at present used for manufacturing their nitric esters all over the world. Glycol dinitrate, or nitroglycol, is the most important

additive to nitroglycerine in the preparation of low-freezing dynamites. The marked volatility of this substance precludes its use for the production of smokeless powder.

Diglycol (2,2′-dihydroxydiethyl oxide) is also used as a substitute for glycerine. Diglycol dinitrate, or dinitrodiglycol, is less volatile than nitroglycol and most of it is utilised for the production of smokeless powder.

ETHYLENE GLYCOL MONONITRATE

$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2OH \end{array}$$

Glycol mononitrate (mononitroglycol) is a by-product accompanying the nitration of glycol in the manufacture of nitroglycol (glycol dinitrate). Mononitroglycol is a liquid with a boiling point of 91–92°C under a vacuum pressure of 10 mm Hg. Its specific gravity at 20°C is 1.35, its viscosity being slightly higher than that of nitroglycol. Mononitroglycol is soluble in water and in most organic solvents. It readily dissolves collodion cotton. It is powerful enough explosive, its heat of explosion is 855.6 kcal/kg (water as vapour) and in the lead block test it produces an expansion of 375 cm^3 [4].

Mononitroglycol may be obtained in a manner analogous to the Mikołajczak process. Glycol is dissolved in 3 parts of nitric acid (density 1.51 g/cm^3) at a temperature of 0°C, the solution is poured onto ice and neutralized with a sodium carbonate solution. An oil consisting of glycol mononitrate (75%) and dinitrate (25%) separates [4]. From this oil mononitroglycol is extracted with water and purified by distillation under reduced pressure. The mononitrate can be further purified by re-dissolving in water and re-distillation. The yield of mononitrate is about 52% of theoretical. Mononitroglycol can be obtained from ethylene oxide and dinitrogen tetroxide. Nitrito-nitrate is formed and then the O-nitroso group is hydrolysed with sodium carbonate solution [39].

The simpliest laboratory method of preparing mononitroglycol consists in reacting ethylene bromohydrin with silver nitrate [5] in acetonitrile solution [6]:

$$\begin{array}{l} CH_2Br \\ | \\ CH_2OH \end{array} + AgNO_3 \longrightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2OH \end{array} + AgBr \qquad (2)$$

ETHYLENE GLYCOL DINITRATE ("NITROGLYCOL")

$$\begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array}$$

Physical properties

Ethylene glycol dinitrate (EGDN, GDN, or nitroglycol respectively) is a transparent liquid characterized by the following physical parameters: freezing point —22.3 or —22.8°C; boiling point 197.5, 105.5 (19 mm Hg) or 70°C (2 mm Hg);

density 1.5176 (at 0), 1.496 (at 15) or 1.489 g/ml (at 20°C). The latent heat of fusion of the frozen product is 30 kcal/kg. Nitroglycol, like nitroglycerine, is fairly soluble in the majority of organic solvents except carbon tetrachloride and petrol in which it dissolves to a smaller extent. Water mixes with it slightly more readily than with nitroglycerine. The solubility of nitroglycol in 100 ml of water varies with temperature (Naoúm [4]):

at 15°C	0.62 g
20°C	0.68 g
50°C	0.92 g

Other authors [40] quote the following value:

at 0°C	0.57 g

Nitroglycol dissolves collodion cotton with the greatest ease even in the cold, in this respect performing better than nitroglycerine. Nitroglycol is practically non-hygroscopic, and is significantly more volatile than nitroglycerine.

Different authors have published divergent values for the volatility of nitroglycol. Thus Moreschi [7] reported a vapour pressure of 0.3 mm Hg at 20°C. According to Rinkenbach [8] at a temperature of 22°C the vapour pressure is 0.0565 mm Hg. The data quoted are cited both by Naoúm and Meyer [9] and by Crater [10]. The most accurate values are those published by Marshall [11] for the temperature range 0–100°C:

temperature, °C	0	20	40	60	80	100
pressure, mm Hg	0.0044	0.038	0.26	1.3	5.9	22.0

According to the work of Brandner [12] the vapour pressure of nitroglycol at different temperatures is as follows:

temperature, °C	20	30	40	50
pressure, mm Hg	0.048	0.125	0.299	0.648

The vapour pressure of solutions of nitroglycol in nitroglycerine has been reported on p. 44 (Table 13).

In a publication of Rinkenbach [13] the volatility of nitroglycol was reported to be 2.2 mg/cm^2/hr. This value is 20 times greater than that for nitroglycerine. Since it possesses a sufficiently high vapour pressure at 100°C nitroglycol can be slowly steam distilled.

The viscosity of nitroglycol is appreciably lower than that of nitroglycerine (Moreschi [7]). At 15°C it amounts to 0.08056 P while at 40°C it is 0.02831 P. Rinkenbach [8] has reported a viscosity of 0.0363 P at 23.6°C the corresponding viscosity of nitroglycerine being 0.288 (and that of water 0.01 P), while in more recent data by the same author [13] a value of 4.2 cP (0.042 P) at 20°C is reported. The refractive index (n) is:

temperature, °C	0	15	25	35
n	1.4546	1.4491	1.4454	1.4417

Values for the physical constants of ethylene glycol dinitrate found by de Kreuk [14], and Boileau and Thomas [15] are given in Tables 2 and 3 respectively (p. 3). Dipole moments are given in Table 4 (p. 4).

Chemical stability

Like nitroglycerine, on heating with aqueous solutions of sodium or potassium hydroxides, nitroglycol is hydrolysed. In contact with an alcoholic solution of potassium hydroxide, it reacts vigorously to yield potassium nitrite and potassium glycolate.

Again like nitroglycerine, it is hydrolysed to some extent by hot water, the degree of hydrolysis (0.008% of the substance at 60°C during 5 days) being rather more marked than that of nitroglycerine. This is most probably due to the higher solubility of nitroglycol.

Like nitroglycerine, nitroglycol decomposes on prolonged contact with concentrated acids. Nevertheless numerous experiments have shown nitroglycol to be more stable than nitroglycerine. Thus when maintained at a temperature of 75°C the first symptoms of decomposition do not occur until after 11 days' heating. In spite of this nitroglycol usually fails to pass a heat test at 72°C. This is due to its high volatility and hydrolysis of the product that condenses on the potassium iodide–starch paper. Heating to a temperature of 195–200°C provokes an explosion less violent than that of nitroglycerine.

The activation energy E of the thermal decomposition of nitroglycol has been estimated:

by Apin, Khariton and Todes [16] as 35.0 kcal/mole

by Andreyev *et al.* [17] as 35.7 kcal/mole

(for the coefficient B the authors found values of $\log_{10} B = 14$ and 14.3 respectively).

Explosive properties

Nitroglycol is a powerful high explosive, which detonates with complete decomposition:

$$\begin{matrix} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{matrix} \longrightarrow 2CO_2 + 2H_2O + N_2 \qquad (3)$$

Owing to thorough utilization of the carbon, hydrogen and oxygen the thermal effect of explosion is larger than in the case of nitroglycerine. An explosion of 1 kg nitroglycol is accompanied by the evolution of 1580 kcal (water vapour) or 1705 kcal (condensed water), i.e. 7% more than that produced by nitroglycerine. The heat of formation $-\Delta H_f$ of nitroglycol is 67.7 kcal/mole.

Nitroglycol is less sensitive to impact than nitroglycerine. It explodes under a 2-kg weight falling from a height of 20–25 cm.

According to Andreyev's [17] experiments when contacted with a flame nitroglycol behaves in a slightly different way from nitroglycerine: it burns quietly at atmospheric pressure. In glass tubes 4 mm dia. within a pressure range of 300–770

mm Hg at 14–15°C, its burning rate increases linearly with the pressure, in accordance with the equation

$$U = A + Bp$$

Burning ceases as soon as the pressure drops below 230 mm Hg.

The same linear relation between the rate of burning and the pressure holds for values up to 10 kg/cm^2, after which a further increase in pressure causes a faster increase in the rate of burning, until detonation occurs.

Analysis of the combustion products of nitroglycol obtained at atmospheric pressure (Altukhova and Andreyev [18] indicates a high content of NO (nearly all the nitrogen being present in that form), and of CO_2, CO and CH_4.

The combustion of large amounts of the substance can lead to explosion. Liquid nitroglycol is more readily initiated by means of a detonator than liquid nitroglycerine, and explosive combinations containing nitroglycol behave similarly.

Nitroglycol, like nitroglycerine, can detonate with high or low velocity. The following figures indicate the rate of detonation:

TABLE 20

DATA CHARACTERIZING THE DETONATION RATE OF NITROGLYCOL

State of aggregation	Method of loading	Initiation	Rate m/sec	Author
liquid	in an iron pipe, 32–38 mm dia.	No. 8 detonator	7830	Naoúm and Berthmann [19]
liquid	in an iron pipe 32–38 or 35–43 in. dia.	80 g picric acid	8200–8300	Naoúm and Berthmann [19]
liquid	in a crucible	No. 8 detonator	1000–3000	Stettbacher [20]
solid (−70°C)	in a crucible	No. 8 detonator	over 8000	Stettbacher [20]

In a lead block with water tamping nitroglycol causes an expansion of 650 cm^3, i.e. 110% of that produced by nitroglycerine.

The biological properties of nitroglycol resemble those of nitroglycerine, but the effect caused by breathing the vapour of nitroglycol is usually stronger, on account of its higher volatility and hence its higher concentration in air, though less persistent for the same reason of higher volatility [21].

Manufacture of nitroglycol

The first papers discussing methods of preparing glycol dinitrate from glycol and its properties were published by Champion [22] and Henry [5]. At that time they were only of theoretical interest in the absence of economic methods of preparing ethylene glycol. According to a report by Kekulé [23] published as early as 1869, by passing ethylene through a mixture of nitric and sulphuric acids an oily

substance was obtained which was hydrolysed in the presence of water vapour to form nitric acid, oxides of nitrogen, glycolic acid and oxalic acid. By reduction with sodium amalgam, a certain amount of glycol and ammonia were obtained. It was not until 1920 that Wieland and Sakellarios [24] made it clear that the components of Kekulé's oil were: nitroglycol (glycol dinitrate) (I) and nitric ester of β-nitroethyl alcohol, i.e. β-nitroethyl nitrate (II). They suggested that the reaction of nitrating ethylene proceeds as defined by equations (4) and (5).

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + \begin{array}{l} HO \\ | \\ NO_2 \end{array} \longrightarrow \begin{array}{l} CH_2OH \\ | \\ CH_2NO_2 \end{array} \xrightarrow{+\,HNO_3} \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2NO_2 \end{array} \quad \text{II} \tag{4}$$

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2HNO_3 \xrightarrow{-H_2O} \begin{array}{l} CH_2ONO \\ | \\ CH_2ONO_2 \end{array} \xrightarrow{HNO_3} \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \quad \text{I} \tag{5}$$

Fifty to sixty per cent of ethylene reacts in accordance with eqn. (4), and 40–50% in accordance with eqn. (5). Numerous attempts to use an oil comprising a mixture of (I) and (II) in the manufacture of explosives have been unsuccessful, because β-nitroethyl alcohol nitrate is insufficiently stable. Experiments have been made to partially hydrolyse the oil with hot water at 80–90°C. Under these conditions nitroethyl nitrate undergoes decomposition, whereas nitroglycol remains unchanged (Oehme [25]). However, the method was not adopted in practice because the yield of nitroglycol is relatively low, i.e. about 40% by weight of the oily product.

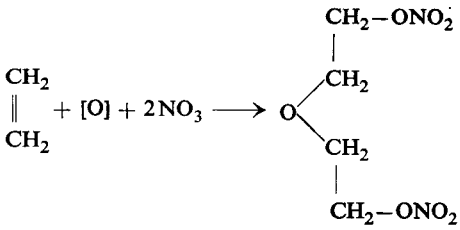
Finally in 1920 Oehme proposed a method for the nitration of ethylene oxide, whereby an oil composed mainly of nitroglycol is produced. Unfortunately, the quality of the product is appreciably impaired by other products which are formed simultaneously, hence the method was not accepted by the industry.

A later method proposed by Oehman [26] produces glycol nitrate and diethylene glycol from ethylene by electrolysis. A platinum wire mesh submerged in an acetone solution of calcium nitrate acts as anode, ethylene being blown through the solution continuously. The cathode space behind the aluminium cathode is filled with a solution of calcium nitrate in nitric acid. At the anode the nitrate ion forms a free radical NO_3 which combines partially with ethylene to produce nitroglycol (6);

$$\begin{array}{l} CH_2 \\ \| \\ CH_2 \end{array} + 2NO_3 \longrightarrow \begin{array}{l} CH_2ONO_2 \\ | \\ CH_2ONO_2 \end{array} \tag{6}$$

According to Oehman a proportion of the free nitrate radicals reacts with one another according to reaction (7) probably accompanied by the evolution of oxygen that combines with NO_3 radicals to form diethylene glycol dinitrate, as outlined in eqn. (8):

$$2NO_3 \longrightarrow N_2O_5 + [O] \xrightarrow{+\,H_2O} 2HNO_3 \longrightarrow 2NO_3 \tag{7}$$



(8)

The anode liquor is neutralized by means of calcium hydroxide, and acetone is removed by distillation. The residue consists of calcium nitrate and glycol dinitrate. These are separated by filtering and the product is washed with water in the usual way. For a certain time this method was used industrially.

In the present time nitroglycol is produced in exactly the same way as nitroglycerine.

Particularly extensive investigation into the kinetics of ethylene glycol nitration have been carried out by Oehman *et al.* [40, 41], Roth, Stow and Kouba [27]. The mixed acid ranged in composition from 11.5 to 20% of water, 18–40% of HNO_3 and 45–68.5% of H_2SO_4. The ratio of mixed acid to ethylene glycol weight ranged from 12 to 24.

Roth *et al.* found that with mixed acids containing less than 15% water, conversion of glycol to ethylene glycol dinitrate was quantitative. Increase in the temperature of the nitrator content can serve as a criterion of the progress of the reaction.

The heat evolution of the reaction is strongly influenced by the amount of water in the mixed acid (Fig. 65). The bottom curve (mixed acid with 20% H_2O) has practically no slope. In these experiments no glycol dinitrate was obtained. The initial increase of temperature here is probably due to the heat of solution of glycol in mixed acid followed by slow nitration.

The heat of nitration ΔH_n from the equation: Glycol + $2HNO_3$ (liq.) $\longrightarrow$ $\longrightarrow$ GDN + $2H_2O$ (liq.) + ΔH_n was found to be 8.5 kcal/per mole of glycol.

The reaction carried out in larger equipment duplicated the data found on a small scale.

The reaction is virtually finished after 1–1½ sec.

The manufacture of nitroglycol on an industrial scale consists in the nitration of glycol in the same type of plant as those used for the production of nitroglycerine.

German standards [28] require that glycol used for nitrating should correspond to the following conditions: the limits of boiling temperature to be 196–200°C, density 1.1130–1.1135 g/cm^3 (20°/4°), acidity below 0.1, and saponification value below 1.0 (Na_2O).

In consequence of the slightly different properties of the raw materials and the products, there exist some divergencies in the course of nitrating glycol as compared with glycerine nitration. No pre-heating of the glycol is necessary before nitration, since the viscosity of glycol is appreciably lower than that of glycerine. The heat produced during the nitration of glycol is a little less than with glycerine, and the slightly higher nitration rate makes the process quicker. Furthermore, it is possible

to use more intensive cooling without any danger of freezing the product. The optimal temperature of nitrating is 10–15°C, higher temperature reduces the yield.

In view of the higher solubility of nitroglycol in water as little water as possible should be used for washing. Both for the above reason and because of the higher volatility of nitroglycol, the use of very warm wash water should be avoided. In order to minimize the loss caused by the volatility of nitroglycol gentle stirring with water and neutralizing solutions by means of compressed air must be carried out with care. This does not exert any adverse effect on the purity of product, because the viscosity of nitroglycol is lower than that of nitroglycerine and vigorous stirring is not necessary.

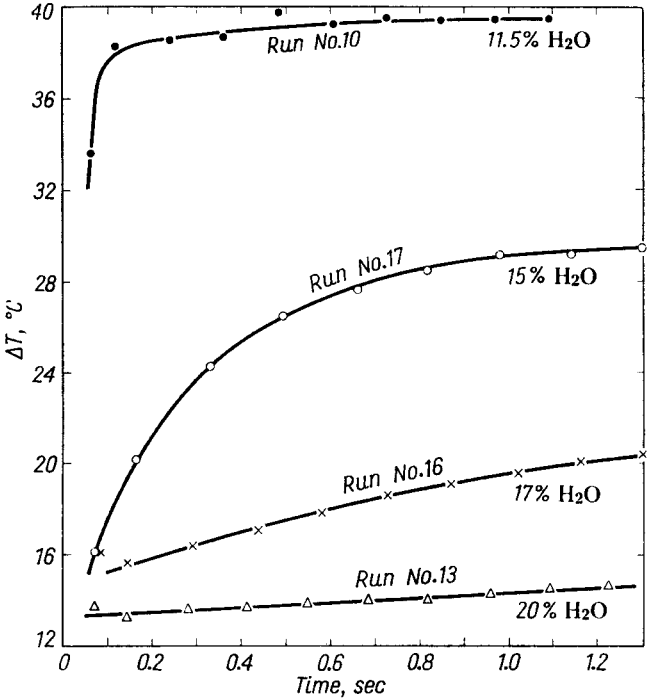


FIG. 65. Heat evolution on nitration of ethylene glycol with nitrating mixtures of variable water content (Roth, Stow and Kouba [27]).

Ropuszyński [29] reports a more elevated temperature for nitrating glycol giving a product containing less residual acid (as observed by the same author in the case of nitroglycerine)—Table 21.

TABLE 21

Temp. of nitration °C	Residual acid content		Heat test min
	% HNO_3	% H_2SO_4	
15	0.0088	0.0015	16
25	0.0041	0.0010	18

Since nitroglycol is more soluble and more volatile a marked loss of product occurs so that the yield of nitroglycol is relatively lower than that of nitroglycerine. 100 kg of glycol at 10–12°C yield 222 kg of nitroglycol, i.e. 90.5% of the theoretical yield of 245 kg.

Handling the spent acid from nitroglycol manufacturing is appreciably safer than handling spent acid from the manufacture of nitroglycerine, since nitroglycerine remains longer in contact with spent acid than nitroglycol. This factor, plus the lower sensitiveness of nitroglycol to impact and its smaller tendency to explode by ignition combine to make the manufacture of nitroglycol less dangerous than the production of nitroglycerine. That there is less danger of nitroglycol contacting spent acid as compared with nitroglycerine can also be seen from the diagram of Oehman, Camera and Cotti [42] (Fig. 26, p. 84).

In practice a mixture of glycerine and glycol in a 50/50 ratio is usually nitrated, so as to produce in one operation a product suitable for use in low-freezing dynamites.

DIETHYLENE AND TRIETHYLENE GLYCOL ESTERS

DIETHYLENE GLYCOL DINITRATE

$$CH_2ONO_2{-}CH_2{-}O{-}CH_2{-}CH_2ONO_2$$

Diethylene glycol dinitrate is also known as diglycol dinitrate and DEGDN (dinitrodiethylene glycol) or, more exactly, di-(ethyl-2-ol) ether dinitrate or 2,2′-dihydroxydiethyl ether dinitrate. Its commercial names are: Dinitrodiglycol, Nitrodiglycol and DNDG. In English speaking countries the abbreviations DEGDN, DGDN or DEGN are commonly used.

Physical properties

Dinitrodiglycol exists in two crystalline forms — a stable form melting at a temperature of +2°C and a labile one whose melting point is —10.9°C (thus resembling nitroglycerine). At 20°C it is an oily liquid of density 1.385 g/cm^3, boiling and simultaneously decomposing at 160°C. Its refractive index is 1.4517 (at 20°C).

Dinitrodiglycol is more volatile than nitroglycerine. Its vapour pressure is 0.0036 mm Hg at 20°C and 0.130 mm Hg at 60°C. Its volatility at 60°C is 0.19 mg/cm^2/hr.

Dinitrodiglycol dissolves in nitroglycerine, nitroglycol and in some organic solvents. It is scarcely miscible with ethyl alcohol, carbon tetrachloride and carbon disulphide. The solubility in 100 g water is 0.40 g at 25°C and 0.46 g at 60°C. Oehman [43] and Aubertein [44] made a detailed investigation of the solubility of dinitrodiglycol in mixed acids (Fig. 66).

Hackel and Kuboszek [30] have examined the eutectics of both forms of DEGDN with *sym*-trinitrobenzene and α-trinitrotoluene (Table 22).

Collodion cotton is very readily dissolved in diethylene glycol dinitrate, more so than in nitroglycerine. The viscosity of diethylene glycol dinitrate at 20°C is 8.1 cP, i.e. lower than that of nitroglycerine.

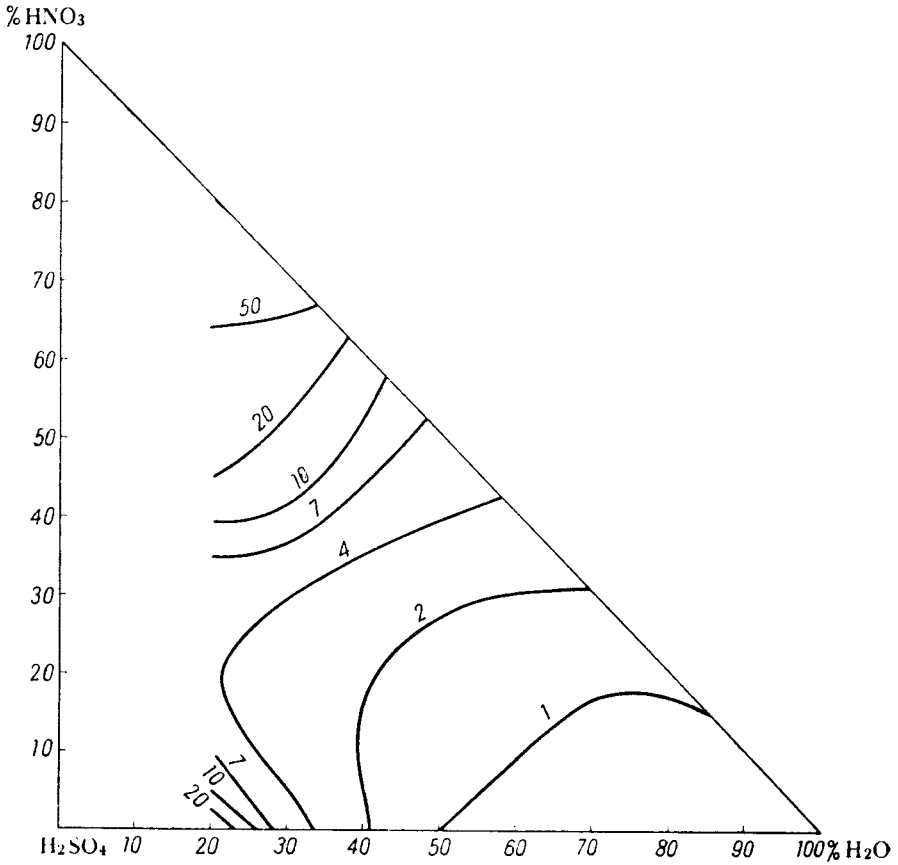


FIG. 66. Solubility of DEGDN in mixed acids [44].

TABLE 22

The second component	Eutectics			
	Stable form		Labile form	
	% of the second component	freezing temp. °C	% of the second component	freezing temp. °C
TNB	8.0	−13.2	11.5	−1.4
TNT	17.0	−15.5	20.5	−3.0

Stability and thermal decomposition

The chemical stability of dinitrodiglycol resembles that of nitroglycerine. Heated with water it undergoes hydrolysis more slowly than nitroglycerine: on being maintained for 5 days at 60°C only 0.003% is decomposed. Hydrolysis in the presence

of acids (Fig. 67) or sodium hydroxide is also more difficult. On the other hand dinitrodiethylene glycol decomposes more readily than nitroglycerine when exposed to action of spent acid probably due to the presence of ether-oxygen in the molecule.

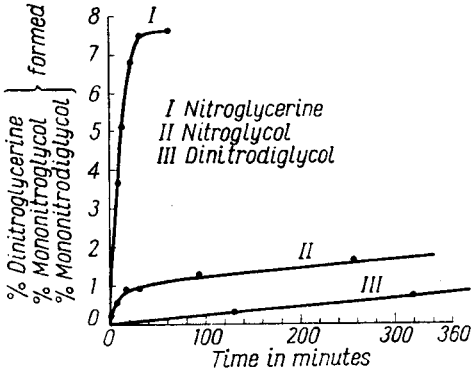


FIG. 67. Rate of denitration of nitroglycerine, nitroglycol and dinitrodiglycol with mixed acid containing 7.5–10.5% HNO_3 and 0.5–1.1% H_2O (Oehman [43]).

The relation between the chemical stability and nitrating temperature observed by Ropuszyński [29] in the instance of nitroglycerine (p. 43) and nitroglycol (p. 148) has been also confirmed with dinitrodiglycol. Diglycol nitrated at a higher temperature demonstrates improved stability owing to its lower content of residual acids. The relevant data are shown in Table 23.

TABLE 23

THE RELATION BETWEEN THE NITRATING TEMPERATURE AND RESIDUAL ACID CONTENT

Nitrating temperature °C	Residual acid content		Heat test min
	%HNO_3	%H_2SO_4	
15	0.138	0.0025	22
25	0.0069	0.0015	30

Dinitrodiglycol is as toxic as nitroglycerine. It explodes at a temperature of 200°C developing a relatively small heat of detonation that amounts to 1070 kcal/kg. Advantage is taken of this property in the manufacture of flashless and non-errosive low calorific smokeless ("double base") powder.

Dinitrodiglycol is incomparably less sensitive to shock than nitroglycerine, in this respect approaching nitrocompounds, such as TNT. It explodes on impact with a 2-kg weight dropped from a height of 160 cm. It is ignited by a direct flame with some difficulty and having been ignited it does not explode like nitroglycerine.

It follows from the investigations of Andreyev [17] that dinitrodiglycol is less capable of burning than nitroglycerine. Thus in glass tubes of 5–6 mm dia. it does not burn at 15°C. To obtain burning the tube diameter must be increased to 8 mm or the initial temperature to 40°C. The linear velocity of burning is at that time only half that of nitroglycol.

The increments of pressure required to increase the velocity of burning can be determined by the following equation:

$$U = 0.0162 + 0.0122p$$

At a pressure of 55 kg/cm^2 the burning acquires a pulsating character and its velocity increases rapidly. This behaviour is similar to that of the majority of nitric esters.

Explosive properties

Dinitrodiglycol detonates either at a high velocity of 6800 m/sec, or at a low velocity of 1800–2300 m/sec. Its ability to detonate is less than that of nitroglycerine. Its lead block expansion value is 425 cm^3, i.e. about 70% that of nitroglycerine.

Diglycol dinitrate is widely used in the explosives industry owing to its excellent capacity of dissolving nitrocellulose, the relative safety of handling it and most of all to its comparatively low price, which is less than that of nitroglycol and only slightly higher than that of nitroglycerine. Its weak point is its particular tendency to decompose in the presence of acid, so that storing spent acid is more dangerous than in nitroglycerine manufacture.

Methods of production

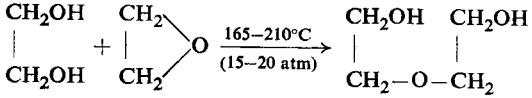
The raw material for the production of dinitrodiglycol, i.e. diethylene glycol, was synthesized as early as 1859 by Wurtz who saturated water and glycol with ethylene oxide at a temperature of 100°C. He tried to nitrate diethylene glycol, but the reaction yielded solely oxidation and hydrolysis products: glycolic acid, oxalic acid and other acids, probably because the temperature was too high. Rinkenbach [8a] published the first description of the properties of dinitrodiethylene glycol, while the industrial nitration process was originally reported by Rinkenbach and Aaronson [31]. These authors established that the largest yield was obtained by using a mixture of acids composed of

50%	HNO_3
45%	H_2SO_4
5%	H_2O

in the proportion of 367 parts of mixed acid to 100 parts by weight of diethylene glycol at a temperature of 10–15°C.

In this way, from 100 parts of diethylene glycol, these authors obtained 158 parts of the product. This is 85.4% of the theoretical yield. Laboratory scale nitration can give 93% yield [42].

In the factory at Krümmel [28] the first stage of manufacturing dinitrodiethylene glycol was the conversion of glycol and ethylene oxide into diethylene glycol according to the equation:



(9)

Diethylene glycol was separated from the reaction product by fractional distillation. Its properties should meet the following standard requirements. It must be an odourless, transparent, colourless or slightly coloured liquid, with a specific gravity of 1.1157–1.1165 at 20°C and maximum water content of 0.5%. Under a pressure of 760 mm Hg 99 parts by weight should distil within temperatures of 241.0°C (at the beginning of distillation) and 246.5°C, the residual 1% coming over below 250°C. The whole distillation should take 25 min. (For barometric pressure a correction of 0.05° for every millimeter of mercury is applicable). Acidity lower than 0.02% (as H_2SO_4) is required, the saponification value may be up to 0.05% (as Na_2O), chlorides can be present only in traces, reducing agents must be absent and the maximum permissible glycol content is 2%.

Diethylene glycol is highly hygroscopic (more so than ethylene glycol), and so must be stored in sealed containers. The viscosity of diethylene glycol is a little higher than that of ethylene glycol, but it is appreciably less viscous than nitroglycerine, hence it is not necessary to heat diethylene glycol before feeding it into the nitrator.

At Krümmel [28] the mixed acid composed of

65%	HNO_3
35%	H_2SO_4

was prepared by mixing nitric acid of 98–99% with oleum 26% and with sulphuric acid. The nitrating acid should be freed from oxides of nitrogen as carefully as possible.

The nitration was carried out by a batch method, each charge comprising 420 kg diglycol and 1218 kg mixed acid. As a safety precaution for storing the spent acid, an excess of 293 kg HNO_3 was added to the mixed acid (theoretically 499 kg of HNO_3 are necessary for nitrating 420 kg of diglycol).

The nitration process was performed in the usual equipment, controlling the temperature, which should not exceed 25°C, by cooling with a 35% sodium nitrate solution, the temperature of which was −15°C. Under these conditions nitration lasted about 25 min. When the nitration was completed, the contents of the nitrator were cooled down to 15°C and transferred to a separator. The separation was accomplished within 7 min and the spent acid was immediately sent to the denitration unit. Special care had to be taken to ensure that no spent acid remained in the tank, because decomposition of the residual dinitrodiethylene glycol may start within a few hours. None the less such decomposition is less hazardous than that of nitroglycerine, since dinitrodiethylene glycol produces a spontaneous explosion only in the instance when the tank is confined.

The spent acid consisted of:

HNO_3	28–29%
H_2SO_4	44–46%
H_2O	20–24%
Dinitrodiglycol	4–5%

The high proportion of nitric acid in the spent acid inhibits hydrolytic decomposition of DEGDN.

Diethylene glycol dinitrate was washed twice after separation, the primary washing being carried out with some 300 l. of water, to give an acid wash water containing

3–4%	HNO_3
5%	H_2SO_4
2–3%	dinitrodiglycol

When the dinitrodiglycol has been separated, the washings were transferred for denitration.

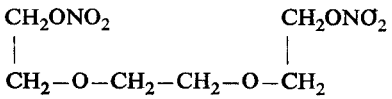
For the second, final washing, 500 l. of cold water were used, after which the product is neutralized with 150 l. of a 5% sodium carbonate solution heated to a temperature of 60°C, and then washed using 500 l. of water.

A sample of dinitrodiglycol subjected to the heat test should withstand a temperature of 82°C for 20 min. Should the product fail the test washing with sodium carbonate solution and water should be repeated.

From each nitration charge 710–715 kg of dinitrodiethylene glycol were produced, i.e. about 92% of the theoretical yield.

TRIETHYLENE GLYCOL DINITRATE

Triethylene glycol dinitrate (dinitrotriethylene glycol, nitrotriglycol, dinitrotriglycol or triglycol dinitrate):



is an oily liquid, with a specific gravity of 1.335. It is characterized by a wholly insignificant sensitiveness to shock, resembling that of dinitrobenzene. Its stability is similar to that of dinitrodiethylene glycol. Its heat of detonation is 750 kcal/kg.

The raw material for manufacturing dinitrotriethylene glycol i.e. triethylene glycol ("triglycol"), should meet the following requirements. It should be a transparent liquid of yellowish colour, with a faint smell. It should not contain glycol and the maximum content of water should be 0.1%. Specific gravity should be 1.1217 at 20°C, and the refractive index at 20°C should be 1.4552. On distillation 95.2 parts by volume should distill over within the temperatures range of 278.8 to 310°C, leaving a solid residue not exceeding 0.001%. Maximum acid content should be 0.005% (as H_2SO_4), the maximum saponification value 0.632% (as Na_2O), chlorine may be present only in traces, and reducing agents must be absent.

According to information from the factory at Krümmel [28] triethylene glycol was nitrated with an acid mixed in the proportion:

HNO_3	70%
H_2SO_4	30%

For a 500 kg charge of triglycol, 1250 kg of nitrating acid were used, nitration being carried out during a period of 30 min.

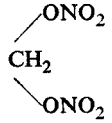
The solubility of dinitrotriethylene glycol in the spent acid is exceptionally high amounting to 8–9%. Denitrating such an acid can be hazardous in view of the presence of such a large amount of an explosive substance. Separation takes place slowly and lasts over half an hour. This is an added hazard, since dinitrotriglycol readily decomposes in the presence of spent acid. It is therefore necessary to add water to the spent acid before the oily explosive material is separated, and the residual spent acid is transferred to the denitration unit. The separated oil is washed twice with water, then with a sodium carbonate solution and finally with water. A sample of washed and neutralized triethylene glycol dinitrate should withstand the heat test for 20 min at 82°C.

From 500 kg of triglycol, 650 kg of dinitrotriethylene glycol, i.e. 72.6% are obtained.

A laboratory scale reaction can give 86–87% yield [43].

ESTERS OF OTHER GLYCOLS

METHYLENE GLYCOL DINITRATE



Methylene glycol dinitrate, or "nitromethylene glycol", is an oily liquid having a boiling point of 75–77°C at 20 mm Hg.

It is a strong explosive, capable of dissolving collodion cotton. However it is not stable, being readily hydrolysed and therefore it is of no practical significance.

A method of obtaining this explosive, by the nitration of moist paraformaldehyde was patented by Travagli and Torboli [32]. They utilised the well-known property of formaldehyde of reacting like methylene glycol in the presence of water.

According to Travagli [33] methylene glycol dinitrate is obtained as follows: paraformaldehyde is dissolved in sulphuric acid and added drop-wise at 3–5°C into a mixture of nitric and sulphuric acid. The resulting oil is separated and washed with water to give a final yield of 35%.

TRIMETHYLENE GLYCOL DINITRATE

Trimethylene glycol dinitrate, 1,3-propylene glycol dinitrate (1,3-propanediol dinitrate) or nitropropylene glycol

$$O_2NO-CH_2-CH_2-CH_2-ONO_2$$

is an oily liquid boiling at 180°C under 10 mm Hg, with a specific gravity of 1.393 at 20°C. It is more volatile and less viscous than nitroglycerine. It is miscible with the same solvents as nitroglycerine. It dissolves collodion cotton fairly well. For the various physical constants of 1,3-propylene glycol dinitrate (such as viscosity, refractive index, dielectric constant, dipole moment) — see Tables 2, 3, and 4 (pp. 3 and 4).

Concentrated nitric acid decomposes it with oxidation.

The chemical stability of trimethylene glycol dinitrate is excellent. A sample kept at a temperature of 75°C for a period of 25 days does not decompose. In the heat test, the iodide–starch paper is coloured only because of the volatility of the substance.

Nitropropylene glycol is a strong explosive. According to Naoúm [4] the heat of detonation is 1138.5 kcal/kg (water as vapour). When heated it explodes at 225°C. Its sensitiveness to impact is very low: a 2-kg weight falling from a height of 100 cm fails to initiate an explosion. According to Naoúm it gives an expansion of 540 cm^3 in the lead block with water tamping, which is equivalent to 90% of that produced by nitroglycerine. The expansion produced by a 93% blasting gelatine made from trimethylene glycol dinitrate is 470 cm^3, i.e. 80% of the effect produced by the same gelatine made from nitroglycerine.

Trimethylene glycol dinitrate aroused interest during World War I, since a considerable amount of trimethylene glycol occurs in glycerine obtained by the fermentation method. Furthermore glycerine may be converted to trimethylene glycol by bacterial action, as demonstrated by Freund [34] as early as 1881. It has been established that the amount of glycol formed during glycerol fermentation is insignificant and that it is formed mainly from glycerine as a result of secondary fermentation processes. A high concentration of sulphite in the fermentation vats prevents the formation of glycol, but its formation is stimulated by decreasing the sugar content of the mash.

Most of the trimethylene glycol can be separated from glycerine by distillation since glycol has a significantly lower boiling point.

The presence of glycol does not have any adverse effect on nitration, it merely reduces the yield.

Pure trimethylene glycol boils at 211°C, its specific gravity is 1.0526 (at 18°C). Trimethylene glycol distilled from fermentation glycerine contains a certain amount of sulphur compounds (0.6–0.7% expressed as sulphur).

According to Naoúm [4] the nitration of trimethylene glycol requires a lower temperature than that used for nitrating glycerine, because the central methylene group is readily oxidized at a higher temperature. A temperature between 0 and 10°C is recommended since decomposition is possible even at 15°C, while at 20°C yellow fumes are evolved. Separating the product from the spent acid occurs with ease at 10°C. From 100 parts of trimethylene glycol, 198 parts of dinitrate are produced corresponding to 90.6% of the theoretical yield.

The spent acid behaves differently from that remaining after the nitration of

nitroglycerine, since after an interval of time the glycol dinitrate contained in the solution undergoes oxidation, accompanied by a temperature rise of as much as 30°C and by the evolution of oxides of nitrogen, and carbon dioxide.

As shown by Naoúm [4] a mixture of glycerine with 5–10% trimethylene glycol can be nitrated without difficulty at 30°C, the mixture behaving like pure glycerine. Nevertheless, if the proportion of trimethylene glycol amounts to 20%, the inclination to oxidation is evident initially at a temperature of 20°C but if the reaction is carefully controlled it is possible to perform the nitration at 25°C. The spent acid that remains after nitrating such mixtures behaves like the acid resulting from the nitration of glycerine, except that its content of NO_2 developed by the oxidation processes is greater.

METHYL GLYCOL DINITRATE

$$\begin{array}{l} CH_3-CHONO_2 \\ \quad\quad | \\ \quad CH_2ONO_2 \end{array}$$

Methyl glycol dinitrate (propylene-1,2-glycol dinitrate or 1,2-propanediol dinitrate) is an oily liquid, boiling at 92°C at 10 mm Hg. Its specific gravity is 1.368 (at 20°C). The liquid does not freeze at a temperature of —20°C. It is more volatile than the isomeric propylene-1,3-glycol dinitrate.

Various physical constants of 1,2-propyleneglycol dinitrate (such as viscosity, refractive index, dielectric constant, dipole moment) are given in Tables 2 and 4 (pp. 3 and 4).

In physical properties and explosive parameters methyl glycol dinitrate resembles its isomer. The heat of detonation as 1110 kcal/kg (water as vapour). The expansion produced in the lead block with water tamping is 540 cm^3 [4].

As early as in 1904 the substance was proposed [35] as an additive to lower the freezing temperature of nitroglycerine, but its practical application on a large scale was hindered by lack of the raw material, propan-1,2-diol. It is only recently that the synthesis of glycol from ethylene led to the development of a method for producing methyl glycol from propylene via chlorohydrin. Even so, propylene-1,2-glycol is somewhat more expensive than glycols derived from ethylene.

1,2-Propylene glycol was nitrated by Naoúm [4] using mixed acid composed of

40%	HNO_3
60%	H_2SO_4

at a temperature of 20°C to produce 187 parts of product from 100 parts of glycol, i.e. an 86% yield.

A mixed acid containing

47.5%	HNO_3
45.5%	H_2SO_4
7%	H_2O

was used by Matignon, Moureau and Dode [36] at 10°C. By using 10% excess of HNO_3 they achieved a yield of 91–93%.

1,3-BUTYLENE GLYCOL DINITRATE

$$CH_3{-}CHONO_2{-}CH_2{-}CH_2ONO_2$$

Butylene-1,3-glycol dinitrate (1,3-butanediol dinitrate), also called "dinitrobutylene glycol", is an oily liquid (at 15°C) which does not freeze at a temperature of —20°C. Its specific gravity is 1.32. Dinitrobutylene glycol is more volatile than nitroglycerine, but less so than nitroglycol. Collodion cotton dissolves in it fairly easily [4,37].

For other physical constants of 1,3-butanediol dinitrate see Tables 2 and 4 (pp. 3 and 4).

The substance is characterized by excellent chemical stability. Its explosive strength, as measured by the expansion produced in the lead block, is equivalent to about 75% of the explosive strength of nitroglycerine.

As early as in 1911 butylene-1,3-glycol dinitrate was suggested [38] as a component of explosives either alone or blended with nitroglycerine.

Its raw material, 1,3-butylene glycol, is produced from acetaldehyde by conversion into acetaldol and reduction to the glycol:

$$2CH_3CHO \longrightarrow CH_3 \cdot CHOH \cdot CH_2 \cdot CHO \longrightarrow CH_3CHOH \cdot CH_2 \cdot CHOH \qquad (10)$$

Naoúm [4] nitrated 1,3-butylene glycol and obtained a yield of 93.7%, i.e. from 100 parts of butylene glycol, 187.5 parts of dinitrate were obtained. (See also Matignon *et al.* [36], Aubry [37]). Aubertein [42], however, pointed out the difficulty of nitrating 1,3-butylene glycol with nitric–sulphuric acid mixtures.

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CHAPTER VI

MONOHYDROXYLIC ALCOHOL ESTERS

METHYL NITRATE

FOR a long time methyl nitrate CH_3ONO_2 has aroused interest, for it is the simplest ester of nitric acid and at the same time one of the strongest explosives. However, its high volatility and low boiling point prevented practical application until World War II, though it was used in the nineteenth century for a certain time in the organic chemical industry as a methylating reagent, e.g. instead of methyl sulphate. This application soon ceased owing to the danger of handling the substance. During World War II, it was used in Germany under the name myrol as a rocket fuel.

PHYSICAL PROPERTIES

Naoúm [1] describes methyl nitrate as a colourless liquid boiling at 65–66°C, very mobile and possessing a viscosity lower than that of water. Its specific gravity is 1.21.

Pauling and Brockway [2] established the structure of methyl nitrate and the length and bond angles, using the electron diffraction method (p. 2).

It is slightly miscible with water: 100 ml of water dissolve 3.85 g of methyl nitrate at room temperature. Methyl nitrate is capable of dissolving collodion cotton and higher nitrated cellulose with the greatest ease. It has a distinctive, agreeable odour. Breathing vapours of methyl nitrate causes headaches. The physiological action is similar to the effect of inhaling nitroglycerine, with the difference that the symptoms are noticeable in a very short time and that they disappear more swiftly. Vapours of methyl nitrate are inflammable: heating to a temperature of 150°C causes explosion.

Many investigations have been made into the mechanism of its explosive decomposition in the gaseous phase on heating to a sufficiently high temperature, e.g. 250–300°C, or by a spark or irradiation.

STABILITY AND THERMAL DECOMPOSITION

Decomposition of methyl nitrate under these conditions produces a spontaneous explosion. Apin, Khariton and Todes [3] on the basis of original experiments

in this field, suggested that the spontaneous decomposition is caused by the exothermic character of the reaction:

$$2CH_3ONO_2 \longrightarrow CH_3OH + CH_2O + 2NO_2 \quad (1)$$

The explosion of gaseous methyl nitrate subjected to the influence of an electric spark at 25°C was investigated by Zeldovich and Shaoulov [4] who found that it differs from an explosion initiated by heat. According to these authors, the following equations express the decomposition reaction caused by an electric spark:

$$\text{induction: } CH_3ONO_2 \longrightarrow CO + NO + H_2O + \tfrac{1}{2}H_2 \quad (2)$$

$$\text{explosion: } CH_3ONO_2 \longrightarrow \tfrac{1}{2}CO + \tfrac{3}{2}H_2O + \tfrac{1}{2}CO_2 + \tfrac{1}{2}N_2 \quad (3)$$

The thermal decomposition of methyl nitrate has been studied by Phillips [5], who suggested that the reactions occurring at the initial stages of decomposition of methyl nitrate and of other simple nitric esters are as follows:

$$RCH_2ONO_2 \rightleftarrows RCH_2O^{\ominus} + NO_2 \quad (4)$$

$$RCH_2O^{\ominus} + RCH_2ONO_2 \longrightarrow RCH_2OH + \overset{\ominus}{R}CHONO_2 \quad (5)$$

$$\overset{\ominus}{R}CHONO_2 \longrightarrow RCHO + NO_2 \quad (6)$$

$$R{-}CH_2O^{\ominus} \longrightarrow \tfrac{1}{2}R{-}CHO + \tfrac{1}{2}R{-}CH_2OH \quad (7)$$

Alternate oxidation and reduction reactions take place between the products to form such gases as nitrous oxide and carbon monoxide.

Gray and Rogers [6] have studied the decomposition of methyl nitrate induced both thermally and by irradiation. They postulate that a spontaneous decomposition occurs at 300°C, in the following stages: initiation of the reaction according to eqn. (2) is followed by oxidation reactions:

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (8)$$

$$2NO + 2CO \longrightarrow 2CO_2 + N_2 \quad (9)$$

$$2NO + 2H_2 \longrightarrow 2H_2O + N_2 \quad (10)$$

Summing up, decomposition may be formulated in a single equation:

$$CH_3ONO_2 \longrightarrow 0.95\ NO + 0.025\ N_2 + 0.75\ CO + 0.25\ CO_2 + 0.7\ H_2 + 0.8\ H_2O \quad (11)$$

The reaction induced by an electric spark proceeds according to the following equation:

$$CH_3ONO_2 \longrightarrow 0.175\ NO + 0.41\ N_2 + 0.49\ CO + 0.51\ CO_2 + 0.175\ H_2 + 1.31\ H_2O \quad (12)$$

As for the reaction occurring as the result of irradiating methyl nitrate Gray and Rogers suggest that this chemical change may be expressed by means of the equation:

$$CH_3ONO_2 \longrightarrow 0.30\ NO + 0.35\ N_2 + 0.50\ CO + 0.50\ CO_2 + 1.2\ H_2O + 0.30\ H_2 \quad (13)$$

Gray and Rogers are of the opinion that free radicals take part in all explosive decomposition reactions of methyl nitrate.

The thermal effect from exploding methyl nitrate (1609–1612 kcal/kg) is 1% higher than that developed by the explosion of nitroglycerine according to equations:

$$2CH_3ONO_2 \longrightarrow CO_2 + CO + 3H_2O + N_2 \quad (14)$$

$$\text{and } 2CH_3ONO_2 \longrightarrow 2CO_2 + 2H_2O + H_2 + N_2 \quad (15)$$

(Berthelot [7]).

Methyl nitrate is less sensitive to impact than nitroglycerine: it detonates under the impact of a 2-kg weight falling from a height of 40 cm. Andreyev and Purkaln [8] established that it burns in a glass tube at atmospheric pressure with a linear velocity of about 0.12 cm/sec, i.e. about 4 times faster than nitroglycerine. Burning continues to take place quietly under increased pressure until a value of 1.5 kg/cm^2 is exceeded. Under higher static pressures, pulsation becomes visible and further increase of pressure, e.g. up to 4 kg/cm^2 may produce explosion.

For pressures within the range 0.175–2.0 kg/cm^2, the linear velocity of burning may be estimated from the equation

$$U = 0.010 + 0.133\ p$$

EXPLOSIVE PROPERTIES

The sensitiveness of methyl nitrate to shock produced by detonation is one of highest ever known — it is appreciably higher than that for nitroglycerine. Thus, detonation of methyl nitrate can be initiated even by a No. 1 detonator. The lead block expansion with water tamping was found to be (Naoúm [1]):

520 cm^3 with a No. 1 detonator (nitroglycerine 190 cm^3)
615 cm^3 with a No. 8 detonator (nitroglycerine 590 cm^3)

The excellent aptitude to detonate may be explained to some extent by the exceptionally low viscosity of the substance. Similarly the low viscosity of methyl nitrate favours a high detonation rate.

Berthelot [9] has published some data concerning the rate of detonation of methyl nitrate. They are listed below:

in a glass tube dia. 3/12 mm	2480 m/sec
in a glass tube dia. 3/7 mm	2190 m/sec
in a steel tube dia. 3/15 mm	2085 m/sec

In a tube 30–40 mm dia. the detonation rate is 8000 m/sec. In a small diameter tube a detonation rate of about 1500 m/sec has been found, while in a wide tube detonation is propagated at a rate exceeding 6000 m/sec (Ratner [10]).

MANUFACTURE

On a small scale methyl nitrate can be obtained by carefully distilling a mixture of methyl alcohol with nitric acid containing urea nitrate [18] or with nitric–sulphuric acid mixture at 40 or 18°C [19].

Commercial quantities are manufactured in a way similar to nitroglycerine, except

that because of the high volatility of methyl alcohol and methyl nitrate, the contents of the nitrator should not be stirred by compressed air. Thus Schmid system nitrators with mechanical stirrer were used in Germany during World War II [11]. Also, on account of the low boiling point and high volatility of methyl nitrate, hot water is not used for washing. Its low viscosity enables the product to be washed thoroughly with cold water and cold solutions.

100 parts of methyl alcohol yield 200 parts of methyl nitrate, i.e. 83% of the theoretical yield.

ETHYL NITRATE, $C_2H_5ONO_2$

PHYSICAL AND THERMOCHEMICAL PROPERTIES

Ethyl nitrate is a liquid boiling at 87°C, with a specific gravity of 1.12. It is scarcely miscible with water, but readily dissolved by organic solvents. Collodion cotton is dissolved in it with ease.

The substance aroused interest as long ago as in Berthelot's [7] day. He determined the O-nitration heat of ethanol as 6.2 kcal/mole. Thomson [12] has estimated the heat of combustion $-\Delta H_c$ to be 324.04 kcal/mole.

Naoúm [1] investigated its explosive properties (see further) and reported the heat of explosion to be 816 kcal/kg (water as liquid). Despite the fact that its appreciable explosive properties had long been recognized, no further attention was paid to ethyl nitrate for some time, because there seemed no possibility to finding a practical use for it. Very recently, however, it has been used as an ingredient of liquid rocket fuels. This has stimulated investigations designed to determine its properties more accurately.

Thus the heat of explosion (under oxygen-free conditions) has been determined by Wheeler, Whittacker and Pike [13] to be $-Q = 77.6$ kcal/mole, i.e. 853 kcal/kg, which is close to the value reported by Naoúm [1].

From the thermochemical data quoted, Gray, Pratt and Larkin [14] have calculated both the heat of formation of ethyl nitrate at 25°C and other thermochemical constants including the latent heat of evaporation. These data are collected in Table 24.

TABLE 24

THERMOCHEMICAL PROPERTIES OF ETHYL NITRATE

Property in question	Amount of heat
Heat of formation of the liquid substance at 25°C $-\Delta H_f$	45.7 kcal/mole
Heat of formation of the gaseous substance $-\Delta H_f$	37.0 kcal/mole
Latent heat of evaporation (ΔH_v) at 25°C	8.7 kcal/mole
Latent heat of evaporation (ΔH_v) at boiling point	8.1 kcal/mole
Entropy (in relation to absolute zero) of the liquid substance at 25°C	59.08 cal/mole/degree
Entropy of formation of the liquid at 25°C	−118.1 cal/mole/degree
Gibbs free energy of formation ΔF_f° of the liquid substance at 25°C	−10.5 kcal/mole

These authors have also determined the vapour pressure over the range 0 to 68°C. They found the following values:

temperature °C	0	20	30	40	50	60
pressure, mm Hg	16.3	49.9	81.8	129	197	292

These values fit the equation of Antoine

$$\log_{10} p \text{ (mm)} = 7.145 - \frac{1329}{t°C + 224°C}$$

EXPLOSIVE PROPERTIES

According to Naoúm [1] the expansion produced by ethyl nitrate in the lead block with water tamping is 345 cm^3, the rate of detonation in wide diameter tubes being of the order of 6000–7000 m/sec. Médard [15] has reported that the substance can be detonated in thick-walled metal tubes by strong initiation, for instance by about 40 g of PETN. Using a tube of 27 mm inner dia., the rate of detonation was found to be 5800 m/sec, while in a tube 60 mm diameter it was 6020 m/sec. Attempts to detonate ethyl nitrate in glass tubes 10 mm dia. were unsuccessful. The lead block expansion caused by explosion of ethyl nitrate is about 20% greater than that of picric acid. According to Médard the sensitiveness of ethyl nitrate to shock is not very high: drop tests with a 2-kg weight falling from a height of 50 cm caused explosion in 50%.

The use of ethyl nitrate as a component of rocket fuel involves the problem of thermal decomposition. Levy [16] has studied the decomposition of ethyl nitrate in the gaseous phase, in the temperature range 161 and 201°C under a pressure of a few centimeters of mercury. He found that ethyl nitrite is the main decomposition product. By-products include methyl nitrite, nitromethane, nitrogen dioxide and nitrous oxide.

At 181°C the yield of nitromethane corresponds to 8–9% of the decomposed ethyl nitrate.

Nitromethane and methyl nitrite are probably synthesized from free methyl radicals which react with NO_2.

Using their own data on the decomposition of ethyl nitrate between 180 and 215°C under pressures of 30–50 mm Hg, Adams and Bawn [17] have calculated the activation energy E and the constant B:

$$E = 39.90 \text{ kcal}, \qquad \log_{10} B = 15.8$$

Ethyl nitrate is produced [1] by disssolving ethyl alcohol in the cold in concentrated nitric acid (density 1.41 g/cm^3) free from nitrogen oxides followed by distillation of the product.

In the presence of nitrogen oxides, ethyl alcohol is readily oxidized to acetaldehyde and this chemical change can upset the nitration reaction, if the acid contains appreciable amounts of nitrogen dioxide.

n-PROPYL NITRATE, $n\text{-}C_3H_7ONO_2$

n-Propyl nitrate is a liquid boiling at 110.5°C. Its specific gravity is 1.063. Its explosive properties are not marked and it can be detonated only with great difficulty. The calculated heat of detonation is 549 kcal/kg (water as vapour). Expansion in the lead block test is only 15 cm^3, after correction for the expansion produced by the detonator. When mixed with kieselguhr in the proportions of 71.5–28.5, however, it produces a distinct detonation and in a lead block test it gives an expansion of 230 cm^3 [1]. n-Propyl nitrate is prepared in the same way as ethyl nitrate.

ISOPROPYL NITRATE

The boiling point of isopropyl nitrate is 101–102°C. It can only be obtained indirectly from isopropyl iodide and silver nitrate. Direct nitration of isopropyl alcohol is difficult due to oxidation at the carbon atom carrying the secondary hydroxyl group.

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CHAPTER VII

POLYHYDROXYLIC ALCOHOL ESTERS

BUTANE-1,2,4-TRIOL TRINITRATE

$$CH_2ONO_2-CHONO_2-CH_2-CH_2ONO_2$$

BUTANE-1,2,4-TRIOL trinitrate, also called "nitrobutanetriol", is a good solvent of collodion cotton. It is less volatile than nitroglycerine and a chemically stable compound. Its explosive strength is not much inferior to that of nitroglycerine. Its heat of explosion is 1440 kcal/kg [1].

During World War II, it was produced in Germany on a semi-commercial scale.

Its manufacture largely depends on the availability of the raw material, 1,2,4-butanetriol, which is produced from acetylene by a sequence of chemical changes as outlined below [2]:

$$CH{\equiv}CH + 2CH_2O \xrightarrow{Cu_2C_2} HOCH_2-C{\equiv}C-CH_2OH \xrightarrow[H_2SO_4 + HgSO_4]{+H_2O}$$

$$\longrightarrow HOCH_2-CO-CH_2-CH_2OH \xrightarrow{H_2} HOCH_2-CHOH-CH_2-CH_2OH \qquad (1)$$

BUTANE-1,2,3-TRIOL TRINITRATE

$$CH_2ONO_2-CHONO_2-CHONO_2-CH_3$$

Groll [3] suggested the manufacture of butane-1,2,3-triol trinitrate for use as an explosive. The possibility of using it in practice depends upon the industrial synthesis of the raw material, butane-1,2,3-triol. Reppe [2] has suggested the following method:

$$CH{\equiv}CH + CH_3CHO \xrightarrow{Cu_2C_2} CH{\equiv}C-CHOH-CH_3 \xrightarrow{H_2}$$

$$\longrightarrow CH_2{=}CH-CHOH-CH_3 \xrightarrow{HOCl} CH_2OH-CHCl-CHOH-CH_3 \xrightarrow{NaOH}$$

$$\longrightarrow CH_2OH-CHOH-CHOH-CH_3 \qquad (2)$$

ERYTHRITOL TETRANITRATE

Erythritol tetranitrate (butanetetraol tetranitrate), also called "nitroerythrite", is a solid melting at 61°C. It was obtained as early as in 1849 by Stenhouse [4], by dissolving erythritol in nitric acid in the cold and afterwards precipitating the

product by means of sulphuric acid. It is readily crystallized from an alcoholic solution.

According to T. Urbański [5, 6, 7] it forms a number of eutectics with nitro compounds and nitric esters. The composition of some of these and their melting points are given in Table 25.

TABLE 25

The second component	Eutectics		
	Content of erythritol tetranitrate, wt. %	m.p. °C	Literature
p-Nitrotoluene	47	32.4	T. Urbański [5]
m-Dinitrobenzene	70	42.4	T. Urbański [5]
2,4-Dinitrotoluene	61	40.1	T. Urbański [7]
sym-Trinitrobenzene	67	45.8	T. Urbański [7]
Pentaerythritol tetranitrate	95	59.5	T. Urbański [5]

It also forms molecular addition compounds with α-trinitrotoluene and 2,4,6-trinitroanisole (T. Urbański [6, 7]).

Compounds of erythritol tetranitrate:

with 2,4,6-trinitroanisole 2:1 mol., m.p. 61.6°C
with α-trinitrotoluene 4:1 mol., m.p. *ca.* 65.5°C
(non-homogeneous melting)

Its chemical stability and sensitiveness to impact resembles those of nitroglycerine. It is an extremely strong explosive possessing a positive oxygen balance [8]:

$$C_4H_6(ONO_2)_4 \longrightarrow 4CO_2 + 3H_2O + 2N_2 + \tfrac{1}{2}O_2 + 1414 \text{ kcal/kg} \qquad (3)$$

Wide practical application of erythritol tetranitrate has been prevented by the lack of readily available raw material. The main sources of erythritol are certain kinds of moss and sea-weeds, though chemical synthesis from acetylene, according to the following scheme, has been suggested by Reppe [2]:

$$CH{\equiv}CH + 2CH_2O \xrightarrow{Cu_2C_2} HOCH_2{-}C{\equiv}C{-}CH_2OH \xrightarrow{H_2}$$

$$\longrightarrow HOCH_2{-}CH{=}CH{-}CH_2OH \xrightarrow{HOCl + H_2O_2} HOCH_2{-}CHOH{-}CHOH{-}CH_2OH \qquad (4)$$

Nitroerythrite is used in medicine in place of nitroglycerine, its physiological effect being similar but slower and more prolonged.

PENTITOL PENTANITRATES

$$CH_2ONO_2-(CHONO_2)_3-CH_2ONO_2$$

A number of pentitols (xylitol, ribitol and arabinitol) have been nitrated by I. G. Wright and Hayward [9] to yield the pentanitrates.

The melting points of the nitrates are:

ribitol pentanitrate 33.5–34.0°C
xylitol pentanitrate 37–40°C
L-(−)arabinitol pentanitrate 26.5–27.5°C

The pentanitrates can be partially and fully denitrated by warming with pyridine and by hydrogenating with hydrogen over palladium-on-charcoal catalyst respectively. In the latter case the original pentitols were recovered.

D-MANNITOL HEXANITRATE ("NITROMANNITOL")

$$CH_2ONO_2-(CHONO_2)_4-CH_2ONO_2$$

D-Mannitol hexanitrate, "nitromannitol" or "nitromannite" was obtained by Sobrero [10] by nitrating D-mannitol. In view of its high sensitiveness to impact and great ease of detonation Sobrero suggested that it could act as an initiator. However, experiments carried out in the arsenal at Torino, Italy, have not confirmed this. Nitromannitol has also been obtained by Domonte and Ménard [11].

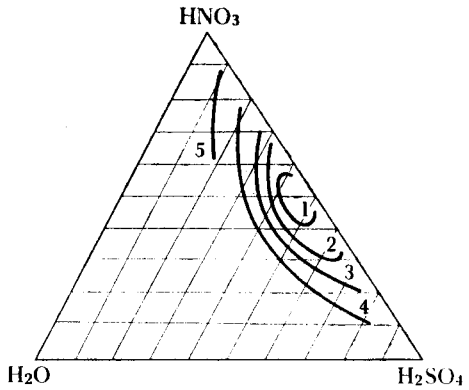


FIG. 68. Nitration of mannitol according to Kunz and Giber [16b]. Nitrogen content: *1*—over 18%; *2*—17.8–18.0%; *3*—17.6–17.8%; *4*—16.6–17.6%; *5*—16.0–16.6%.

Owing to the ease of preparation and purification, the chemical and explosive properties of mannitol hexanitrate have been thoroughly investigated. The following papers are worth attention: Sokolov [12], Berthelot [13], Sarrau and Vieille [14], Wigner [15], C. Taylor and Rinkenbach [16], Médard [16a].

The widest investigation on nitration of D-mannitol in nitric acid–sulphuric acid nitration mixture at 0°C was recently reported by Kunz and Giber [16b]. The authors built a triangle diagram (Fig. 68) known as "Sapozhnikov diagram" described in detail in the chapter dedicated to nitrocellulose (p. 333). The curves of equal

nitrogen content showed shapes similar to those of nitrocellulose. The highest nitrogen content (17.8–18.0%) was obtained with the nitrating mixture of 44% HNO_3, 48% H_2SO_4 and 8% H_2O.

The curves of yield possess a similar shape as those of nitrogen content.

The rate of O-nitration of D-mannitol depends mainly on the activity of nitric acid in the acid mixtures.

PHYSICAL AND CHEMICAL PROPERTIES

D-Mannitol hexanitrate crystallizes from ethyl alcohol in the form of needles melting at 112–113°C. Its specific gravity is 1.604. It is immiscible with water, dissolves readily in ether and hot ethanol and with difficulty in cold ethyl alcohol. With aromatic mononitro compounds, e.g. nitrobenzene, *p*-nitrotoluene, *p*-nitroanisole, α-nitronaphthalene, mannitol hexanitrate forms addition compounds melting in a non-homogeneous way, as shown by T. Urbański [5, 6, 7, 17].

The main data are collected in Table 26.

TABLE 26

Second component	Compound		
	Mole ratio nitro compound : nitromannitol	Bent	
		weight % of nitromannitol	m.p., °C
o-Nitroanisole	2:1	34	45.5
p-Nitroanisole	2:1	58	78
Nitrobenzene	2:1	50	60
α-Nitronaphthalene	1:1	27	56
o-Nitrotoluene	2:1	39	51
m-Nitrotoluene	2:1	43	58
p-Nitrotoluene	2:1	54	71

The thermal analysis of these systems can be represented by a general curve — Fig. 69,

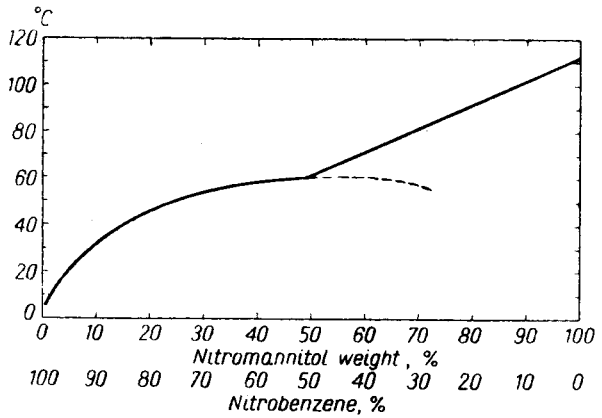


FIG. 69. Nitromannitol and nitrobenzene system melting points (T. Urbański [17]).

Ordinary eutectics are formed by nitromannitol with higher nitrated aromatic compounds (Table 27).

TABLE 27

Second component	Eutectics	
	Weight % of nitromannitol	m.p., °C
m-Dinitrobenzene	52.5	65.5
2,4-Dinitrotoluene	40.0	56.2
sym-Trinitrobenzene	55.0	78.7
α-Trinitrotoluene	42.5	62.8

Heated in a test tube, nitromannitol explodes at a temperature of 160–170°C. There is a divergence of opinion concerning its chemical stability. The stability of a very carefully purified, repeatedly crystallized sample is high, resembling that of nitroglycerine (Guastalla and Racciu [18]). However, a product crystallized only once or twice withstands heating at 75°C for only a few hours, after which brown fumes start to develop.

According to a report of Tikhanovich [19] nitromannitol in contact with an ethereal solution of ammonia undergoes a partial denitration to form D-mannitol pentanitrate (m.p. 81–82°C) together with derivatives of an ether–alcohol mannitane $C_6H_8(OH)_4$, namely mannitane tetranitrate $C_6H_8O(ONO_2)_4$ (an oily liquid) and crystalline mannitane tetramine $C_6H_8O(NH_2)_4$.

Later, Wigner [15] found that by heating with pyridine nitromannitol is denitrated to mannitol pentanitrate, and Hayward [20] has confirmed the denitration to pentanitrate by means of pyridine, occurring even at room temperature. After some 15 hr about a 65% yield is obtained.

Hayward produced evidence that the pentanitrate so obtained has the structure of D-mannitol-1,2,3,5,6-pentanitrate. Methylation of the pentanitrate with silver oxide and methyl iodide gave 4-methyl-D-mannitol pentanitrate (m.p. 111–112°C).

EXPLOSIVE PROPERTIES

Nitromannitol is a strong explosive with a positive oxygen balance. Its decomposition proceeds according to the equation:

$$C_6H_8(ONO_2)_6 \longrightarrow 6CO_2 + 4H_2O + 3N_2 + O_2 + 1512 \text{ kcal/kg}$$

It is initiated by shock as readily as nitroglycerine: a two kilogram weight dropped from a height of 4 cm causes a sample to explode. In direct contact with flame it melts and burns in the open air with difficulty. It burns evenly only after it has been warmed up. Andreyev [21] has reported that nitromannitol burns with appreciably more difficulty than nitroglycerine. In order to cause it to burn in a glass tube it was necessary to heat it to 95°C and to reduce the pressure to 85 mm Hg.

The rate of burning is thereafter rather high: 0.104 g/sec/cm^2, appreciably higher than that of nitroglycerine burning under the same conditions. Once it is kindled mannitol hexanitrate burns rapidly and large quantities may explode. In the lead block with water tamping an expansion of 560 cm^3 is produced, i.e. 93% of that produced by nitroglycerine.

The rate of detonation is:

for a loading density 0.9 g/cm^3
in an iron pipe dia. 25/35 mm 5600 m/sec (Naoúm [8])
for a loading density 1.5 g/cm^3
in an iron pipe dia. 4 mm 7000 m/sec (Berthelot [13])
for a loading density of 1.75 g/cm^3
in an iron pipe dia. 12.8 mm 8260 m/sec (Kast [21a])

Formerly the raw material for the production of nitromannitol, i.e. mannitol, was prepared from the juice of berries, in particular from *Traxinus ornus* (manna). At present it is produced by reducing D-mannose or D-fructose; in the latter case D-sorbitol is also formed.

Nitromannitol can be obtained by nitrating mannitol with a mixture of nitric acid and sulphuric acid. The method is inconvenient, however, since the reaction produces a thick crystalline mass and the nitration proceeds unevenly [8]. Generally therefore, mannitol is dissolved in a five-fold amount of nitric acid ($d = 1.51$) at a temperature below 0°C, which is maintained while a ten-fold quantity of sulphuric acid ($d = 1.84$) is added to the solution. Fine crystals of the product are precipitated which were separated on a vacuum filter. The product is slightly impure due to the presence of mannitol pentanitrate. The acid product is drowned quickly in cold water, filtered again, washed with cold water, neutralized by means of dilute sodium bicarbonate solution and once again washed with water. Nitromannitol is crystallized from alcohol, to which a stabilizer (diphenylamine) is added.

Mannitol hexanitrate is now used as a secondary charge in some detonators, instead of tetryl. Thus it is used in detonators in which the primary initiator is diazonitrophenol. There also exist detonators wherein nitromannitol is used with tetrazene. Such a blend behaves as an initiator.

On crystallization nitromannitol forms needles which easily felt together into an unpourable mass which makes filling the detonators practically impossible. The crystallization process is therefore carried out so as to precipitate the product as granules, by adding protective colloids, triphenylmethane dyestuffs or similar substances.

Nitromannitol is used for medicinal purposes instead of nitroglycerine, since its physiological effect is slower and longer lasting.

DULCITOL HEXANITRATE ("NITRODULCITOL")

Dulcitol hexanitrate, D- or L-galactitol hexanitrate, "nitrodulcite" or "nitrodulcitol", is a crystalline product, melting at 94–95°C. It was obtained as early as 1860 by Béchamp [22]. Dulcitol is an isomer of mannitol, hence the properties of nitro-

dulcite are similar to those of nitromannite (Wigner [15], Taylor and Rinkenbach [16], Patterson and Todd [23]).

Dulcitol occurs in plants (manna from Madagascar). It can also be obtained by reduction of D-galactose or lactose.

The preparation and chemical properties of dulcitol hexanitrate were studied in detail by Hayward and McKeown [24]. They found that the hexanitrate is partly denitrated by warming to 50°C with pyridine. The denitration product was characterized as D- or L-galactitol-1,2,4,5,6-pentanitrate (m.p. 85–86°C).

D-SORBITOL HEXANITRATE

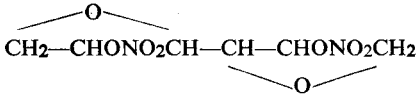
Sorbitol hexanitrate, or nitrosorbitol, is an isomer of nitromannitol. In normal conditions it is a crystalline material melting at 55°C. It has been obtained by Bergheim [25] and by Tettamanzi and Arnaldi [26].

Davis [27] has described its physical state as an oily liquid, which was used in the United States as an additive to nitroglycerine in low-freezing dynamites.

The discrepancy has been explained by the experiments of T. Urbański and Kwiatkowska [28] who found that by dissolving sorbitol in a five-fold quantity of concentrated nitric acid ($d = 1.52$) at 0°C followed by precipitating the product with the help of a ten-fold amount of 20% oleum at +5°C, hexanitrate only slightly contaminated with pentanitrate was formed. When, however, the temperature of nitration and precipitation is −10°C an oily mixture of sorbitol hexa- and pentanitrates was produced. Most probably it was a mixture of this kind that Davis described, as sorbitol pentanitrate exists under normal conditions in the form of an oil. The explosive properties of nitrosorbitol resemble those of nitromannitol.

Sorbitol is at present manufactured commercially by catalytic reduction of D-glucose. Hence the nitrated product may attain greater practical importance.

DINITRATES OF DIANHYDROHEXITOLS



2,5-Dinitrates of 1,4;3,6-dianhydrohexitols have been prepared by Formann, Carr and Krantz [29] in an attempt to obtain vasodilatory substances. Jackson and Hayward [30] studied their chemical properties.

They prepared 1,4;3,6-dianhydrides of D-mannitol, D-glucitol and L-iditol:

isomannide dinitrate, m.p.	64.5–65.5°C
isosorbide dinitrate, m.p.	50.5–51.5°C
iso-idide dinitrate, m.p.	68–69°C

POLYVINYL NITRATE

Attempts to obtain polyvinyl alcohol nitrate, (polyvinyl nitrate), were made with the object of producing a synthetic polymer capable of replacing nitrocellulose.

The earliest experiments began in 1929 when Börschman and Funk [31] dissolved polyvinyl alcohol in concentrated sulphuric acid at a temperature of *ca.* 0°C and then introduced the solution slowly into the nitrating mixture which was heated gradually to 40–50°C, polyvinyl nitrate being precipitated. The originally plastic precipitate, after being filtered and washed changes into a brittle substance which can be pulverized readily. The product contains *ca.* 10% of nitrogen. Burrows and Filbert [32] reacted polyvinyl alcohol with nitric acid at 10–20°C to obtain the nitrate. The authors pointed out that the alcohol is readily oxidized and that measures to counteract this are necessary.

Noma, Oya and Nakamura [33] examined the reaction of nitrating polyvinyl alcohol and concluded that neither nitration with a mixture of nitric and sulphuric acid, nor nitration with nitric and acetic acid can bring about the esterification of all the hydroxyl group. This is probably due to simultaneous hydrolysis. They recommend nitrating either with a composition of nitric acid and acetic anhydride or a solution of nitric acid in carbon tetrachloride, where by a higher nitrated product, softening at a temperature of 40–50°C, is obtained.

According to Deans and Nicholls [34] polyvinyl nitrate of 13–15% N content produced a lead block expansion of 153–342 cm^3 (TNT produced 255 cm^3).

Le Roux and Sartorius [35] have determined the content of nitrogen in polyvinyl alcohol nitrate to be 13.5–14.5%, whereas its theoretical maximum content of nitrogen is 15.75%. The detonation of polyvinyl alcohol nitrate is propagated with a rate similar to that of nitrocellulose of the same nitrogen content. The rate of detonation of polyvinyl nitrate, containing 13.4% of nitrogen, in cardboard cartridges 30 mm dia. is:

at a loading density	
0.3 g/cm^3	2030 m/sec
0.6 g/cm^3	3450–3520 m/sec
1.0 g/cm^3	4920–5020 m/sec
1.4 g/cm^3	6090 m/sec
1.5 g/cm^3	6560 m/sec

Polyvinyl nitrate is a readily inflammable substance which burns without melting. It has not been used industrially on account of its poor chemical stability. Further, unlike nitrocellulose, it cannot form solutions which after evaporation of the solvent, leave a film of high mechanical strength. This is probably the result of lack of orientation of the molecular chains.

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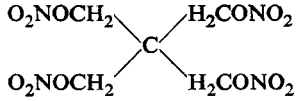
CHAPTER VIII

POLYHYDROXYLIC BRANCHED-CHAIN AND CYCLIC ALCOHOL ESTERS

PENTAERYTHRITOL TETRANITRATE (PETN)



PENTAERYTHRITOL tetranitrate ("nitropentaerythrite") also has numerous trade names which are different in various countries: PETN, Penthrite, Penta (English speaking countries), Pentrit, Niperyth, Nitropenta, NP (Germany), Pentryt, NP (Poland), Ten (U.S.S.R.). PETN was first obtained by the Rheinisch-Westfälische Sprengstoff A.G. in 1894 [1], by nitrating pentaerythritol.

PENTAERYTHRITOL

Pentaerythritol was obtained by Tollens and Wigand in 1891 [2] from acetaldehyde and formaldehyde according to the following reaction:

$$CH_3CHO + 4CH_2O + \tfrac{1}{2}Ca(OH)_2 \longrightarrow C(CH_2OH)_4 + \tfrac{1}{2}(HCOO)_2Ca \qquad (1)$$

Addition of copper salts permits substantial improvement of yield. The reaction appears to proceed in two stages. Initially an aldol condensation occurs between three molecules of formaldehyde and one molecule of acetaldehyde:

$$3CH_2O + CH_3CHO \xrightarrow{(OH^{\ominus})} C(CH_2OH)_3CHO \qquad (2)$$

Afterwards the pentaerythrose reacts with a fourth molecule of formaldehyde according to Cannizzaro's reaction:

$$CH_2O + C(CH_2OH)_3CHO + \frac{Ca}{2}OH \longrightarrow C(CH_2OH)_4 + HCOO\frac{Ca}{2} \qquad (3)$$

This reaction scheme was proposed by Tollens and Wigand [2].

More recent investigations into the mechanism of formation of pentaerythritol have been made both by Wawzonek and Rees [3] and by Barth, Snow and Wood [4]. Both groups tried to explain the process in terms of the formation of *sym*-pentaerythritol ether (dipentaerythritol), and other ethers, e.g. the methyl ether. The latter is produced whenever the formaldehyde used for the reaction contains methyl alcohol:

$$CH_2O + H_2O \longrightarrow HOCH_2OH \tag{4a}$$

$$CH_3OH + HOCH_2OH \longrightarrow CH_3OCH_2OH + H_2O \tag{4b}$$

$$CH_3OCH_2OH + CH_3CHO \xrightarrow{OH^{\ominus}} CH_3OCH_2CH_2CHO$$

$$CH_3OCH_2CH_2CHO + 3CH_2O + NaOH \longrightarrow$$

$$\longrightarrow CH_3OCH_2-\underset{\displaystyle CH_2OH}{\overset{\displaystyle CH_2OH}{\overset{|}{\underset{|}{C}}}}-CH_2OH + HCOONa \tag{4c}$$

Numerous investigations have been carried out with the aim of increasing the yield of pentaerythritol. These are reviewed in the monograph of Berlow, Barth and Snow [5]. Recently the use of basic ion exchange resins instead of calcium hydroxide was recommended [5a]. Some *sym*-pentaerythritol ether (dipentaerythritol) is produced along with pentaerythritol as shown by Friedrich and Brün [6]. The proportion of this substance depends upon the reaction conditions (see p. 195).

In spite of its great explosive strength and high chemical stability large-scale production of PETN could not be achieved until formaldehyde and acetaldehyde became available industrially. Therefore during World War I PETN was only of theoretical interest. During World War II it was used for filling detonators as the secondary high explosive charge instead of tetryl boosters, detonating fuses, small arms (e.g. 20 mm) ammunition and for making blends with various explosives. Some 1440 tons of pentaerythritol tetranitrate per month were produced in Germany during this period.

PETN. PHYSICAL PROPERTIES

PETN is a white crystalline substance which melts at 140–141°C. The melting point of the pure chemical substance is 141.3°C. Its boiling point was reported by Belayev and Yuzefovich [7] to be

160°C at 2 mm Hg
180°C at 50 mm Hg
200°C at 760 mm Hg

The ultra-violet absorption spectrum of a single crystal of PETN is characterized by a marked absorption at wave lengths above 280 mμ (Deb [8], Fig. 70).

PETN usually forms needle or column-shaped crystals, in which state it pours with difficulty. It is however possible to produce cubic crystals, which pour easily, by recrystallization from ethyl acetate. PETN has been subjected to many crystallographic studies. On the basis of X-ray measurements carried out by Booth and Llewellyn [9] the interatomic distances have been shown to be:

$$C-C = 1.50\ Å, \quad C-O = 1.37\ Å, \quad O-N = 1.36\ Å,$$

$$N-O \text{ (nitro group)} = 1.27\ Å$$

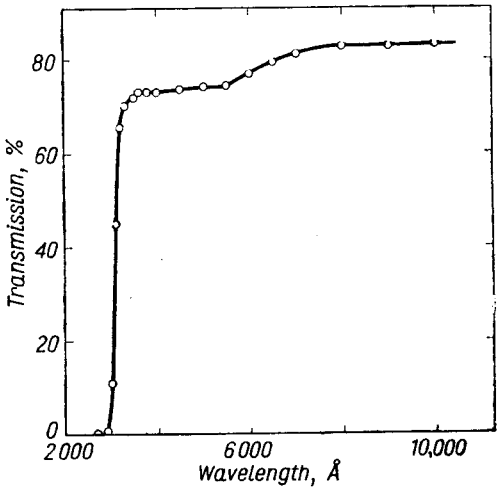


FIG. 70. Ultra-violet absorption spectrum of a single crystal of PETN (Deb, according to Bowden and Yoffe [29]).

The vapour pressure, according Edwards [10], is:

temperature, °C	pressure, cm Hg
97.0	8.38×10^{-5}
110.6	3.12×10^{-4}
121.0	1.09×10^{-3}
131.6	3.76×10^{-3}
138.8	7.08×10^{-3}

From these data Edwards has deduced an empirical equation:

$$\log p = 16.73 - 7750\frac{1}{T}$$

where p — the vapour pressure in cm Hg

T — absolute temperature.

PETN is practically insoluble in water. According to Desvergnes [11], 100 g water dissolve 0.01 g of PETN at 50°C and 0.035 g at 100°C. It is soluble in most

organic solvents. Values for the solubility of pentaerythritol tetranitrate (expressed in g dissolved in 100 g of solution) found by T. Urbański and Kwiatkowski [12] are tabulated in Table 28.

TABLE 28

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE IN ORGANIC SOLVENTS

Temperature °C	PETN (g) dissolved in 100 g of solution				
	Ethyl alcohol	Ether	Acetone	Benzene	Toluene
0	0.070	0.200	14.37	—	0.150
10	0.085	0.225	16.43	0.150	0.170
20	0.115	0.250	20.26	0.300	0.230
30	0.275	0.340	24.95	0.450	0.430
40	—	0.450	—	—	—
40	0.415	—	36.16	1.60	0.620
50	0.705	—	—	2.010	1.100
60	1.205	—	—	3.350	2.490
62	—	—	42.68	—	—
70	2.225	—	—	5.400	3.290
78.4	3.795	—	—	5.400	—
80.2	—	—	—	7.900	—
90	—	—	—	—	9.120
113	—	—	—	—	30.960

Values for its solubility in ethyl acetate and pyridine, as reported by Desvergnes, are given in Table 29.

TABLE 29

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE (DESVERGNES [11])

Temperature °C	PETN (g) dissolved in 100 g of solvent	
	Ethyl acetate	Pyridine
19	6.322	5.436
50	17.868	8.567

It is of special importance for industrial practice to know the solubility of PETN in mixtures of acetone with water. Data reported by Aubertein [13] are listed in Table 30.

The recently published solubility data of Roberts and Dinger [14] agree well with those reported by T. Urbański and Kwiatkowski. The differences are only apparent, owing to the fact that the solubility is reported by the latter authors as grammes of pentaerythritol tetranitrate dissolved in 100 g of solvent (Table 31).

TABLE 30

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE IN ACETONE–WATER MIXTURES (AUBERTEIN [13])

Amount of PETN dissolved in 100 g of solvent	Acetone concentration				
	55%	70%	80%	90%	92%
g	Temperature of solution, °C				
1	41	—	—	—	—
2	52	—	—	—	—
2.5	—	24.5	—	—	—
4	62	—	—	—	—
5	—	41.5	22	—	—
10	—	54.5	38.5	15	10
15	—	62	48	24.5	20.5
17.5	—	65	—	—	—
20	—	—	54	34.5	29
25	—	—	59	41.5	34
30	—	—	63	46.5	40.5
35	—	—	—	51.5	45
40	—	—	—	55	50
45	—	—	—	58.5	54
50	—	—	—	61.5	57.5
55	—	—	—	—	60.5
60	—	—	—	—	62.5

TABLE 31

SOLUBILITY OF PENTAERYTHRITOL TETRANITRATE (AFTER ROBERTS and DINGER [14])

Temperature °C	Acetone	Benzene	Ethanol
15	20.81	—	—
20	24.84	0.275	0.125
25	30.56	—	—
30	34.56	0.496	0.213
40	44.92	0.834	0.378
50	58.76	1.448	0.657
60	—	2.389	1.196

Dimethylformamide is also a good solvent for PETN (Lang [15])

at 40°C 100 g of solution contain 40 g PETN
at 60°C 100 g of solution contain 50 g PETN
at 100°C 100 g of solution contain 70 g PETN

Furthermore, it dissolves in liquid or fused aromatic nitro compounds and in nitric esters to form eutectics. T. Urbański [16] has reported the composition and melting temperatures of the eutectics specified below (Fig. 71).

20% PETN with 80% *m*-dinitrobenzene	m.p. 82.4°C
10% PETN with 90% 2,4-dinitrotoluene	m.p. 67.3°C
13% PETN with 87% α-trinitrotoluene	m.p. 76.1°C
30% PETN with 70% tetryl	m.p. 111.3°C
20% PETN with 80% mannitol hexanitrate	m.p. 101.3°C

Similar systems were examined by Desseigne [105].

According to Hackel [17] PETN forms eutectics with nitroglycerine (see p. 41). With diethyldiphenylurea (centralite I) it produces an eutectic containing 12% of pentaerythritol tetranitrate, melting at 68.0°C.

Ternary systems giving eutectics composed of 16% PETN, 8.5% trinitro-*m*-xylene, 75.5% *m*-dinitrobenzene and 12.5% PETN, 71.0% *m*-dinitrobenzene and

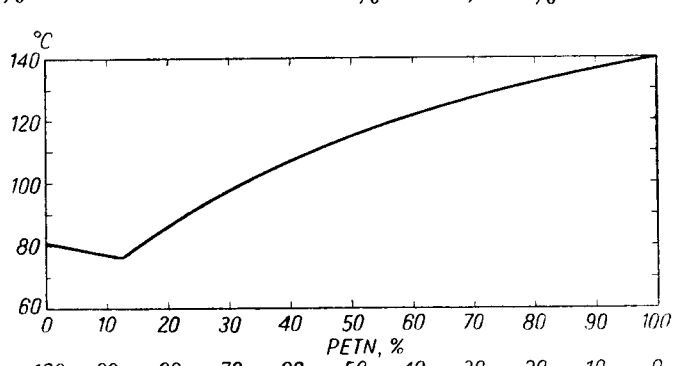


FIG. 71. PETN and TNT system melting points (T. Urbański [16]).

16.5% 1,8-dinitronaphthalene were investigated by Khaybashev and Bogush [18]. The melting points of these eutectics are 79.5 and 69°C, respectively.

PETN differs from other nitric esters in failing to produce a colloid solution with nitrocellulose. This is the result of the symmetrical structure of PETN, which has a zero dipole moment. PETN is completely non-hygroscopic. Its specific gravity in crystalline form is 1.77. On compression the following density values are obtained:

pressure, kg/cm²	density, g/cm³
351	1.575
703	1.638
1406	1.710
2109	1.725
2812	1.740

Ebert, Eisenschütz and Hartel [19] examined the dipole moment of PETN in dilute benzene solution and found it be *ca.* 2.0 D.

Mortimer, Spedding and Springall [20] determined the dipole moments of pentaerythritol and a few of its derivatives including PETN. They found the dipole moment of pentaerythritol to be *ca.* 2.0 D and that of PETN in dioxane $\mu = 2.5$ D.

This led them to conclude that there is free rotation about the C—O bond in the nitrate. It also indicates that the shortening of this bond in crystals observed by

Booth and Llewellyn [9] cannot be due to possession of any marked degree of double-bond character.

The specific heat of pentaerythritol tetranitrate is 0.4 cal/g/°C, the heat of combustion is 1974 kcal/kg, and hence the heat of formation is +390 kcal/kg or $-\Delta H_f = +123$ kcal/mole.

The heat of fusion has been estimated by Roberts and Dinger [14] to be 23–24 kcal/mole. This value has been calculated from experimental solubility data in organic solvents at different temperatures.

The latent heat of sublimation of PETN is 36.3 ± 0.5 kcal/mole (Edwards [10]).

PETN. CHEMICAL PROPERTIES

Due to its symmetrical structure, pentaerythritol tetranitrate is characterized by high resistance to many reagents. Thus PETN, differing from the majority of nitric esters, is not readily decomposed by sodium sulphide at 50°C. On the other hand, it is decomposed quite quickly by boiling in a ferrous chloride solution. Boiling with a 2.5% solution of sodium hydroxide causes very slow decomposition, whereas nitrocellulose rapidly decomposes under these conditions.

Experiments by Aubertein and Rehling [21] have shown that treatment with water at approximately 100°C causes PETN to hydrolyse. At 125°C, and under pressure, hydrolysis proceeds quite quickly, and is considerably speeded up by the presence of 0.1% of HNO_3. Whether it occurs in water alone or in water acidified with nitric acid, the hydrolysis produces mainly pentaerythritol dinitrate. A dilute sodium hydroxide solution causes PETN to hydrolyse more rapidly than acidified water. PETN neither reduces Fehling's reagent nor enters into addition products with any aromatic nitro compound. In this respect it differs from both nitroerythritol and nitromannitol.

The chemical stability of pentaerythritol tetranitrate is very high and exceeds that of all other nitric acid esters. It withstands the heat test at 80°C for several hours. As heating continues decomposition is gradually perceptible at temperatures above the melting point, i.e. above 140°C. Aubertein and Rehling [21] have found that water is occluded in crystals of PETN purified by recrystallization from acetone–water. The presence of these occlusions has an adverse effect on the results obtained by examining the stability of penthrite at 132°C. Removal by grinding and drying the crystals improves the result of the stability test.

It has been established experimentally (T. Urbański, Kwiatkowski, Miładowski [22]) that the addition to pentaerythritol tetranitrate of such nitro compounds as nitrobenzene, nitrotoluene, dinitrobenzene, dinitrotoluene, trinitrobenzene, and trinitrotoluene, decreases its stability as determined by heating to 120–135°C. The degree of decomposition of PETN, heated alone or in mixtures, can be estimated in terms of the pH-values determining the acidity of the decomposition products (Table 32, Fig. 72).

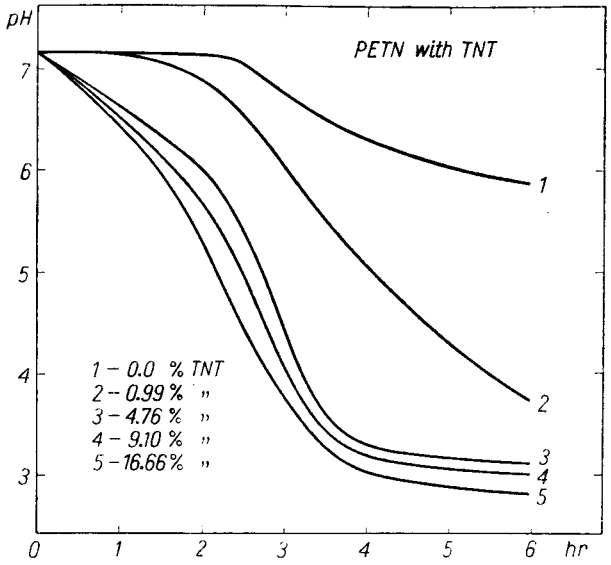


FIG. 72. Change of pH of PETN alone and with TNT on heating at 120°C (T. Urbański, Kwiatkowski, Miładowski [22]).

TABLE 32

CHANGES IN STABILITY OF PETN AT PRESENCE OF ADMIXTURES (T. URBAŃSKI, KWIATKOWSKI AND MIŁADOWSKI [22])

Admixtures	pH-Value of a water extract from the sample kept at 120°C			
	1 hr	2 hr	3 hr	6 hr
Pure PETN	7.16	7.15	6.33	5.86
9.1% *p*-nitrotoluene	5.34	3.50	3.19	1.92
9.1% 2,4-dinitrotoluene	6.30	4.20	3.13	2.92
9.1% α-trinitrotoluene	6.54	5.70	3.32	3.03

Similar results have been found by estimating the time needed to attain a standard pressure (300 mm Hg) due to vapours evolved on decomposition at 134.5°C (the Taliani–Goujon method, p. 28). The following times were recorded (Fig. 73)

for PETN	68.5 min
for PETN with 9.1% *p*-nitrotoluene	26.5 min
for PETN with 9.1% 2,4-dinitrotoluene	27.5 min
for PETN with 9.1% α-trinitrotoluene	30.5 min

The lower stability is probably due to the fall in melting point of pentaerythritol tetranitrate, and hence its transition at a relatively low temperature into the higher energy liquid state.

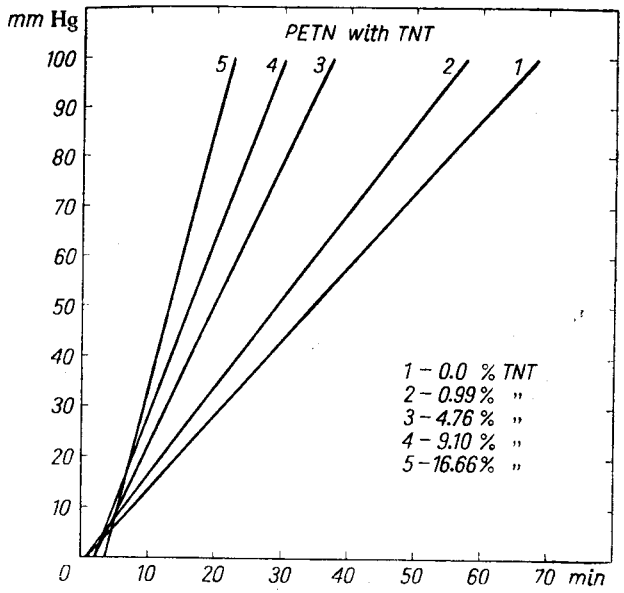


FIG. 73. Pressure evolved by PETN alone and with TNT on heating at 134.5°C (Taliani–Goujon method). (T. Urbański, Kwiatkowski, Miładowski [22]).

Other substances exert a similar influence on the stability of PETN, for example solvents capable of lowering its melting temperature.

The U.S. military specification MIL-P-387 A lays down the following technical conditions for PETN

minimum melting point		140.0°C
minimum nitrogen content		17.50 %
substances insoluble in acetone	max.	0.10 %
acid or alkali content	max.	0.003%

vacuum stability at 120°C, max. 5 ml gas evolved in a 20 hours' test.

The action of PETN on the human system is the same as that produced by all other nitric esters. Nevertheless inhalation of PETN is not dangerous, as its vapour pressure is negligible. Similarly, breathing small amounts of penthrite in the form of dust causes no deleterious effect owing to its low solubility. Lazarev [23] reports the toxicity of pentaerythritol tetranitrate to be lower than that of nitroglycerine.

PETN was introduced into clinical medicine for the treatment of angina pectoris as a long-acting coronary vasodilator [24]. The administration of PETN has very little effect on peripheral arterial vasodilation [25].

PETN. EXPLOSIVE PROPERTIES

Pure PETN heated above its melting point explodes violently at 205–225°C. In the primary stage of thermal decomposition, within the temperature range of 161–233°C, the activation energy E equals 47.0 kcal/mole, while $\log_{10} B = 19.8$, according to A. J. B. Robertson [26].

The following equation of decomposition, using a 1000 g sample of PETN, has been established by A. Schmidt [27]:

$$C_{15.8}H_{25.3}O_{38.0}N_{12.7} = 12.13CO + 3.38CO_2 + 10.35H_2O + 1.71H_2 + 0.1CH_4 +$$

$$+ 0.1C_2H_2 + 0.2NH_3 + 0.1HCN + 6.23N_2$$

heat of explosion 1530 kcal/kg
volume of gases $V_0 = 768$ l./kg
temperature of explosion $t = 4230°C$

It has been found by Haid and Schmidt [28] that the equation of decomposition is practically independent on the loading density. The proportion of gaseous products resulting from the explosive decomposition of PETN under the influence of different stimuli, shown in Table 33, was determined by Bowden and Yoffe [29].

TABLE 33

GASEOUS PRODUCTS OF EXPLOSIVE DECOMPOSITION OF PETN, %

Initiation	NO_2	NO	N_2O	N_2	CO_2	CO	H_2	O_2
Detonation	—	5.3	—	22.8	37.0	26.7	6.8	1.4
Impact	—	24.3	5.3	9.4	19.1	35.4	6.5	—
Thermal decomposition at 210°C	12.0	47.6	9.5	1.6	6.3	21.0	2.0	—

Sensitiveness to shock. T. Urbański [30] has reported that PETN is exploded with a 50% probability on impact by a kinetic energy of 0.20 kgm/cm^2 (in comparison with about 0.95 kgm/cm^3 needed for tetryl). The data of Naoúm [31] and Izzo [32] are similar. Stettbacher [33] on the other hand considered the sensitiveness to impact of PETN to be almost the same as that of tetryl. On account of its relatively high sensitiveness PETN is generally used after being desensitized ("phlegmatized") by adding 10% of montan (lignit) wax. This desensitization has practically no effect on the completeness of detonation.

PETN is not very sensitive to friction but it is characterized by a very high sensitiveness to initiation by explosion. It is detonated by 0.01 g lead azide, the minimum amount required for tetryl being 0.025 g of lead azide. PETN blended with desensitizing agents does not readily lose its aptitude for detonation. Thus, according to the researches of T. Urbański and Galas [34] PETN mixed with 40% of water can be initiated by a No. 8 detonator, which fails to detonate TNT containing barely 15% of water. Thus it is obvious why pentaerythritol tetranitrate detonates with ease when blended with 10% montan wax. On account of its high explosive power and appreciable sensitiveness, PETN is itself an excellent explosive for transmitting a detonation from an initiating explosive to a high explosive charge, i.e. as a "secondary filling" of detonating cups or as a filling for gaines (boosters).

Initiation by an electric spark. PETN can be detonated by a 2000–12000 V electric spark produced by discharging a condenser, as demonstrated by Basset and Basset [35].

Initiation by ultra-violet rays. When a crystal of PETN is subjected for a period of 1.2 msec to an intensive irradiation with ultra-violet rays, producing 900 J of energy, prompt decomposition occurs. Cracks occur on the faces of the crystal resembling those which appear in other explosives as the result of heating. PETN heated to a temperature slightly above its melting point can be exploded however by exposure for 20 μsec to irradiation producing an energy of 480 J (Deb [8]). It is decomposed by irradiation with γ-rays [104, 104a].

PETN ignites with difficulty on contact with a flame, differing this respect from straight-chain nitric esters such as nitroglycerine, nitroglycol etc. In accordance with studies of Andreyev [36] PETN does not burn even in a tube as wide as 18 mm in diameter. Only after pre-heating to 95°C is it possible to induce burning, which proceeds with the extraordinary low linear rate of 0.047 cm/sec. Under a pressure of 20 kg/cm^2 or more, it burns uniformly with a rate depending on the pressure according to the linear relationship:

$$U = 0.02 + 0.0180p$$

The rate of detonation of PETN is 8500 m/sec. Results concerning the detonation rate of pentaerythritol tetranitrate at different loading densities are collected in Table 34.

An increase of the rate of detonation can be achieved by driving out the air retained among the crystals of PETN and replacing it by a non explosive liquid, e.g. water, as shown by the investigations of T. Urbański and Galas [34]. The authors reported detonation rates for charges with a loading density of 1.45 g/cm^3 to be:

for dry PETN	rate of detonation 7295 m/sec
for PETN with 10% of water	rate of detonation 7445 m/sec

for charges with a loading density of 1.40 g/cm^3:

for dry PETN	rate of detonation 7125 m/sec
for PETN with 20% of glycerine	rate of detonation 7825 m/sec

The expansion produced by PETN in the lead block with sand tamping is 500 cm^3 and with water tamping, 560 cm^3. This is equivalent to about 93% of the strength of nitroglycerine or about 170% of that of picric acid.

THE MANUFACTURE OF PENTAERYTHRITOL TETRANITRATE

Of the various methods of manufacturing PETN, the most widely used involves pouring pentaerythritol into nitric acid ($d = 1.50$–1.52) at a temperature not exceeding 25°C. PETN is scarcely soluble in nitric acid. The product which is precipitated towards the end of the nitration, is filtered, washed with water and recrystallized from acetone.

TABLE 34

THE DETONATION RATE OF PENTAERYTHRITOL TETRANITRATE, m/sec

Specific gravity		Roth [41]	Friedrich [40]	Laffitte and Parisot [42][8]	T. Urbański and Galas [34][9]	Cook [43]
0.45		3150[2]				
0.50			3965[4]			
0.76				4200		
0.80				4400		
0.84				4860		
0.85	5330 [31][1]					
0.91		5300[3]		5120		
1.00				5320		5550
1.03			5615[5]			
1.04		5730[3]				
1.22			6355[6]			
1.35					6950	
1.40					7125	
1.45		7375[3]			7295	
1.48	6945 [39]					
1.50			7420[7]			
1.60	7200 [39]					
1.62	8000 [37]		7913[7]			
1.70						8300
1.71	8340 [38]					
1.72		8500[3]				
1.73			8350[7]			
1.75	7750 [39][4]					

1 in an iron pipe, 25 mm dia.
2 in a bakelite pipe 6/8.5 mm dia.
3 in a bakelite pipe 4.5/6.3 mm dia.
4 in a copper pipe, 15/17 mm dia.
5 in a glass pipe, 11.4/13 mm dia.
6 in a copper tube 10/10.6 mm dia.
7 without confinement
8 in a pipe, 6 mm dia.
9 in an iron pipe 21/25 mm dia.

Certain workers (e.g. Stettbacher [44]) have suggested precipitating PETN from nitric acid by adding sulphuric acid at 20°C, filtering the product only after this operation. This method is not to be recommended, since sulphuric acid causes the precipitation of certain impurities dissolved in nitric acid, so that the slight increase in yield is offset by the diminished purity of the product.

Another method suggested by T. Urbański [45] consists in diluting the acid remaining after the nitration with water. If the final concentration of acid is 30–50% HNO_3, complete precipitation of PETN occurs, while the impurities remain in the solution. However, the method can only be used if pentaerythritol of the highest purity is available as the raw material. In practice, two methods are in use: (1)

nitration with nitric acid alone without dilution; (2) nitration followed by dilution with water.

Pentaerythritol destined for the preparation of PETN must be exceptionally pure. In Germany, nitrating grade pentaerythritol ("grade M") had to conform to the following technical specification:

The substance should contain at least 85% of crystals passing through a 2-mm sieve and retained by 0.2-mm sieve. No more than 15% may pass through the latter.

The mineral content	max.	0.5%
moisture content	less than	0.7%
dipentaerythritol content	max.	2%
reducing substances	absent	

A laboratory test nitration should produce a yield over 98%.

Pentaerythritol (LG grade) manufactured by the reaction of formaldehyde and acetaldehyde in the presence of sodium hydroxide at a temperature within the range 10–14 to 37°C was also used for nitrating purposes.

The melting point of pentaerythritol corresponding with the above mentioned specification lies within 250 and 260°C (pure pentaerythritol melts at 261–262°C). To produce it an aqueous solution of acetaldehyde is treated with formaldehyde in the presence of milk of lime, the temperature being gradually increased from 15 to 55°C. When the reaction is complete, the whole is treated with sulphuric acid sufficient to precipitate the lime as calcium sulphate. This is filtered off, and the solution concentrated under reduced pressure. The crystallized product is centrifuged and then recrystallized from water. The yield is about 62% (calculated with respect to acetaldehyde) or 51% if related to formaldehyde.

German method

The nitration of pentaerythritol to produce PETN by a semi-continuous method as used at Krümmel [46] was carried out as follows (Fig. 74).

A nitrator (*1*) of 500 l. capacity is charged with 1000 kg of concentrated nitric acid (98–99%) and 200 kg of pentaerythritol. Nitric acid passes from a storage tank into a metering tank and thence into the nitrator. Pentaerythritol is sucked by vacuum from a storage tank into a metering tank, from which a worm conveyer transfers it to the nitrator. The weighing of the raw materials takes 10 min, the nitration itself about 40 min. A temperature of 15–20°C is maintained in the nitrator by the use of a jacket and of a cooling coil refrigerated by a solution of sodium nitrate (—5 down to —10°C).

Shortly after the nitration has been started a new batch of raw material is weighed and fed gradually into the nitrator so that the contents of the nitrator (*1*) are removed by an overflow to another nitrator (*2*). This unit, with a capacity of 170 l., is cooled by means of a jacket only. In it the incoming product is cooled to 10°C.

The vapours are drawn off the nitrators via a ventilator and flow upwards into a tower where they are sprayed with water, and recovered as 20% nitric acid.

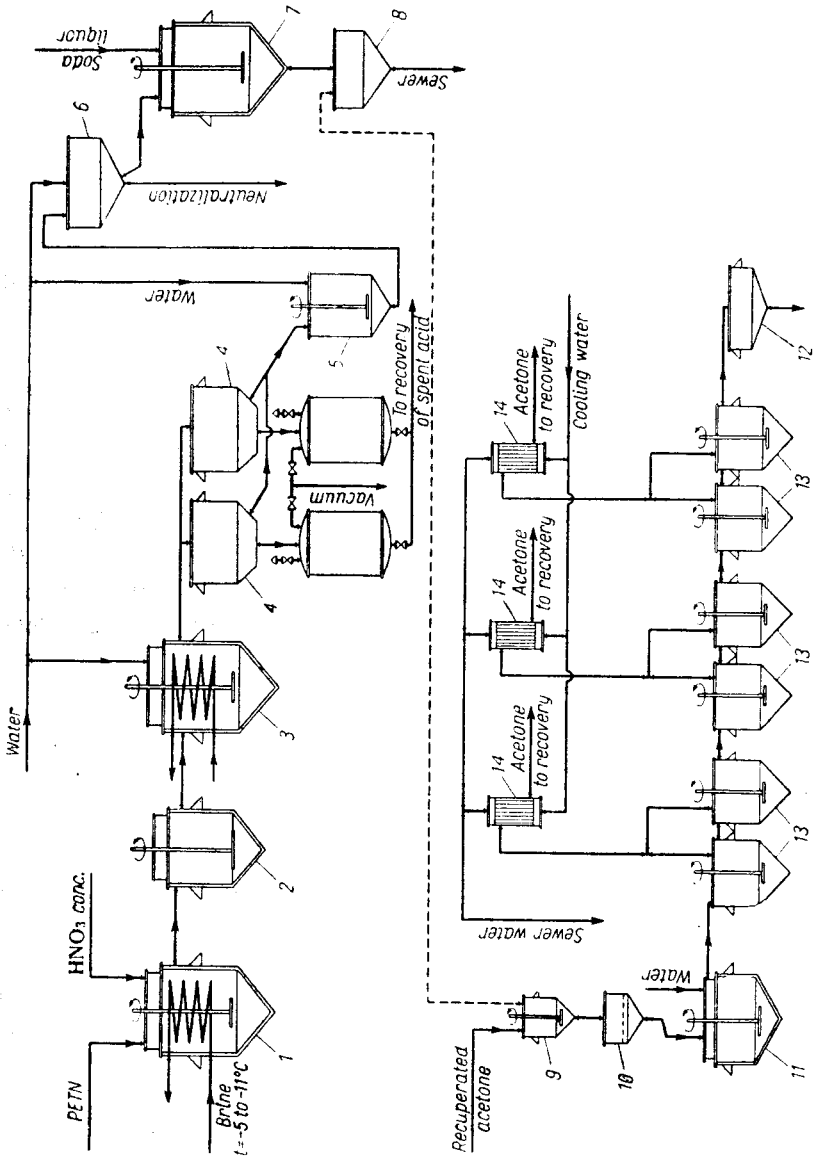


FIG. 74. Flow sheet of continuous manufacture of PETN: *1*—nitrator No. 1, *2*—nitrator No. 2. *3*—diluting vat, *4*—vacuum filter, *5*—washing vat, *6, 8, 10, 12*—filters, *7*—neutralizer, *9*—vat for dissolving PETN in acetone, *11*—diluting vat, *13*—distillation apparatus, *14*—vapour condensers.

In nitrator (*2*) a suspension of PETN-crystals in 80% nitric acid is present. From here the contents pass to diluter (*3*) cooled by a coil and jacket. Here sufficient water is introduced to lower the nitric acid concentration to 30%, while the temperature is kept at 15–20°C.

The suspension of crystals of PETN contained in the diluter flows into one of a batch of vacuum filters (*4*). As each filter is filled with PETN, the stream is directed to another filter, while from the first acid is removed as completely as possible by suction, after which an outlet in the centre of the filter-floor, closed by a conical stopper is opened. The PETN is washed out of the filter with water and carried to a battery of continuously operated washers.

The first unit in the washing installation is a tank (*5*) for washing with water, from which the suspension is pumped to a vacuum filter (*6*) to extract the acid washings. After being washed, the PETN enters a neutralizer (*7*), where it is mixed with sodium carbonate solution at 60°C for 1½ hr. It is then filtered in the vacuum filter (*8*). The liquor from this filter should be alkaline.

The yield of PETN amounts 96.8%, (100 parts of pentaerythritol yield 225 parts of PETN). The raw materials required for the manufacture of 100 kg of PETN are:

	44.4	kg of pentaerythritol
and	224	kg of nitric acid (98–99%)
of which	80	kg enter into the reaction
	16	kg are lost
and	128	kg are recovered as 30% nitric acid.

Afterwards the crude washed PETN is purified by continuous recrystallization. PETN containing about 10% of water is transferred to a tank (*9*), where it is dissolved in acetone at 45°C. A little sodium carbonate is added (for a 200 kg nitration charge of pentaerythritol, 1000 l. of acetone and 3 kg of sodium carbonate are used). After warming up to 50°C the solution is passed through a filter (*10*). After being diluted at 60°C by adding an amount of water to obtain a concentration of acetone of 50–55% the liquor with PETN crystals suspended in it passes to a battery of six stills (*13*) equipped with stirrer and heating jacket, some also having an internal heater. Acetone is distilled off and its vapours condensed in (*14*). In the first still a temperature of 85°C and an acetone concentration of 12–15% is maintained. In the second, 3–5% of acetone is present at 90°C, while in the third, fourth and fifth stills the temperature is 100°C and only traces of acetone remain. As the acetone is distilled off the PETN crystals assume their final shape. PETN purified in this way is separated from water on the filter (*12*). The diluted acetone recovered in the condensers is purified by distillation.

The "phlegmatization" of PETN consists in thorough mixing with montan wax in the proportion of 90% PETN to 10% montan wax [47]. The process is as follows. A mixing tank, equipped with gentle stirrers, is filled with 1200 l. of water heated to 85°C. 315 kg of purified PETN which still contains 10% water is added followed by 250 ml of dilute Sudan red solution intended to distinguish the phlegmatized product, and finally the appropriate amount of melted montan wax. The whole

is stirred for 10 min at 85°C, and then the contents of the vessel are cooled rapidly to 70°C by a spray of cold water. The phlegmatized product is filtered, rinsed with cold water and dried by two stages at 70°C in a convection air drier (ventilation drier). The product is thus dried first to a moisture content of 10–15%, then passed through 4-mm mesh sieve, and finally dried and passed through a 2-mm mesh sieve.

Unphlegmatized PETN is left with a water content of 10–15%, and in this form it is transported and used for the manufacture of mixtures.

Old Soviet method

The method outlined below for the manufacture of PETN was described by Shapshal and Belenkii [48].

A nitrator filled with 300 kg of 93–95% nitric acid is fed with 60 kg pentaerythritol previously dried at 100°C. By means of a cooling jacket a temperature of 20°C is maintained in the nitrator. The equipment is constructed of aluminium, and fitted with a stirrer operating at 120 r.p.m., with a funnel for adding the pentaerythritol and with an outlet for discharging the product at the bottom.

After all the pentaerythritol has been introduced the contents of nitrator are mixed for half an hour, after which the nitration product is allowed to flow to a vacuum filter. As pentaerythritol tetranitrate is present in the form of crystals, filtration is very easy and is complete in about 10–15 min. The concentration of the filtered acid is 78%, while the residual acid content in the separated PETN does not exceed 25%.

The product is transferred to a washing tank of acid-resistant steel, to be drowned in 800 l. of water, and stirred for 15 min. The washer has a double bottom, the upper porous stoneware layer acting as a filter-floor. After being washed PETN is separated on the filter where it is washed again three times with 180 l. batches of water. The washed product contains 1% of acid. It is neutralized in a special tank by means of an eight to tenfold amount of 1% sodium carbonate solution at 85–90°C, the process taking 1 hr before being centrifuged prior to crystallization. At this stage it still contains 0.3–0.5% of acid.

Crystallization is carried out as follows: 2.2 kg of acetone and twice as much sodium carbonate as needed to neutralize the acid contained in the substance are used for every 1 kg of PETN. The solution is warmed to 58°C and stirred at this temperature for 1 hr after which it is passed under a pressure of 1 atm through a filter and into a crystallizer. The filter should be heated to a temperature of 50–55°C, and the crystallizer to 45–50°C. The contents of the crystallizer are cooled very slowly: first at a rate of 1°C per 5 min, later at 2–2.5°C per 1 min. Crystallization is finished within 2 hr.

The crystalline PETN is separated from the solvent in a vacuum filter down to a 15–20% acetone content. The residual acetone is later removed by washing with a small amount of ethyl alcohol. The final product is dried at 40°C. PETN crystallized from acetone should fulfil the following conditions: m.p. 138–140°C, content of moisture and volatile components max. 0.1%, substances unsoluble in

acetone max. 0.1%, mineral content (as ash) max. 0.2%. PETN should be completely free from acid. After keeping a sample at a temperature of 110°C for 8 hr, the pH-value of a water extract should lie between 5.0 and 7.0.

Japanese method

At the Maizuru plant, in Japan [49] PETN was manufactured in World War II in a plant comprising a nitrator lined with acid-resistant steel and provided with a stirrer (140 r.p.m.), a tank made from acid-resistant steel, a centrifuge, a steel crystallizer and unit for recovering acetone.

The nitrator is charged with 825 kg of concentrated nitric acid (98%) and cooled to 10–15°C, after which 150 kg of pentaerythritol are added slowly, while the temperature is kept below 15°C. The addition of pentaerythritol takes about 2½ hr. The contents of the nitrator are then allowed to stand quietly for half an hour before being drowned in some 2000 l. of water.

The aqueous solution of acid is decanted from above the penthrite and run to waste since the acid is too dilute to be worth recovering. PETN is stirred with water which is then decanted. In order to ensure thorough washing this operation is repeated five times. To the last wash aqueous sodium hydroxide solution is added to form a 0.5% solution. Next the PETN is washed again by alternate agitation with water and decantation, four times. An aqueous suspension of the washed product is run into a centrifuge by means of an impeller pump. After being centrifuged, PETN is transported to another building to be purified.

To purify the product, 60 kg of moist PETN are thrown into 150 kg of acetone warmed to 50–55°C and stirred until completely dissolved. The solution is then filtered through a cotton cloth into a vessel filled with 150 l. of water. The precipitated pentaerythritol tetranitrate is centrifuged and dried in a special room for 22 hr at 55°C.

MIXED PENTAERYTHRITOL ESTERS AND ESTERIFIED ETHERS

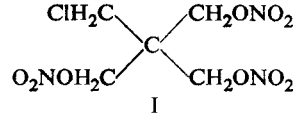
The problem of producing asymmetric pentaerythritol tetranitrate esters of nitric acid, i.e. mixed pentaerythritol esters and pentaerythritol ether esters, is tackled from time to time in investigations which have the dual aims:

(1) To produce explosive derivatives of pentaerythritol less sensitive than pentaerythritol tetranitrate, which could be applied for desensitizing PETN and lowering its melting point, so as to make it possible to fill shells with a molten explosive mixture containing penthrite.

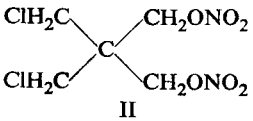
(2) To produce explosive derivatives of pentaerythritol which would have an asymmetrical polar structure, capable of dissolving nitrocellulose. Substances of this kind could find application as components of smokeless powder.

Patents covering a method of producing mixed pentaerythritol esters were published in 1936 by Westfälisch-Anhaltische Sprengstoff A.G. [50]. These substances,

containing two or three hydroxyl groups esterified with nitric acid, possess a lower sensitiveness to impact than PETN. To produce these compounds diesters of acids other than nitric acid are nitrated. For example pentaerythritol mono- or di-chlorohydrin, pentaerythritol mono- or di-formate or pentaerythritol acetate etc. were nitrated. The first two yielded the compounds I and II.



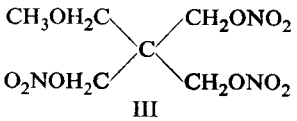
I



II

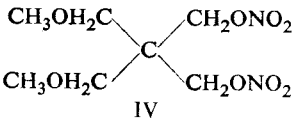
A mixture of the two substances melting at a temperature of 43–50°C gives a lead block expansion 107% that of TNT, and is less sensitive to shock than TNT. (See also Elrick, Gardner, Marans and Preckel [51]).

Particularly interesting properties have been discovered [50] in the pentaerythritol methyl ether nitrates, which are formed by nitrating monomethyl or dimethyl pentaerythritol ether.



III

Monomethyl pentaerythritol ether trinitrate (III) melts at 79–80°C, produces an expansion in the lead block of the same order as TNT, and is less sensitive to impact than TNT.

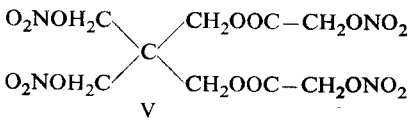


IV

Dimethyl pentaerythritol ether dinitrate (IV) which melts at 53–54°C, produces an expansion in the lead block of about 95% that of TNT. It is insensitive to impact.

Mixed pentaerythritol esters have also been described [50] that contain in their molecule hydroxyl groups substituted by organic acids, which possess nitro groups either in ester form or as C-nitro compounds joined with the acid, alongside simple nitrate ester groups.

Thus, the nitration of glycolic acid pentaerythritol diester yields a tetranitrate (V):

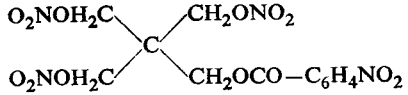


V

This is a liquid explosive. Its strength estimated by the lead block test amounts to about 90% of the strength of TNT.

Nitration of pentaerythritol benzoate causes both esterification of hydroxyl groups with nitric acid, and a simultaneous nitration of the benzene ring to

produce pentaerythritol trinitrate *p*-nitrobenzoate (pentaerythritol trinitrate ester of *p*-nitrobenzoic acid, *p*-nitrophenylenecarbonyl-pentaerythritol trinitrate) (VI):



VI

This is a crystalline substance of great explosive strength, possessing a low sensitiveness to shock.

Pentaerythritol trinitrate esters of nitrobenzoic acid have been also obtained by Marans, Elrick and Preckel [52] who have esterified pentaerythritol trinitrate by means of the corresponding nitrobenzoyl chloride.

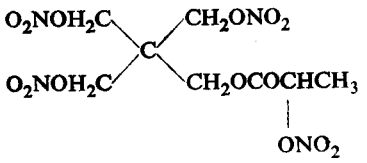
In this way they have prepared, among other esters:

pentaerythritol trinitrate *o*-nitrobenzoate	m.p. 94–95 °C
pentaerythritol trinitrate *m*-nitrobenzoate	m.p. 102–103°C
pentaerythritol trinitrate *p*-nitrobenzoate	m.p. 106–108°C
pentaerythritol trinitrate 3,5-dinitrobenzoate	m.p. 109–110°C

They also prepared pentaerythritol trinitrate formate (m.p. 62–63°C), acetate (87–88°C), propionate (m.p. 39–40°C) and their higher homologues; pentaerythritol trinitrate oxalate (m.p. 97–100°C), glutarate (m.p. 87–88°C), succinate (m.p. 88–90°C), adipate (m.p. 82–83°C), benzoate (m.p. 89–90°C) and phthalate (m.p. 125.0–126.5°C).

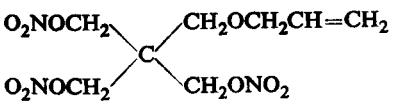
Wagner [53] prepared pentaerythritol dinitrate diacetate and pentaerythritol trinitrate monoacetate and examined their explosive properties.

Wyler [54] suggested to producing mixed esters of nitric acid and of an organic acid also containing a hydroxylic group which would also be esterified by the nitric acid (a similar ester (V) was described above). This method has been applied by Wyler to obtain (nitrate-lactoyl)-pentaerythritol trinitrate, i.e. (α-nitroxypropionyl-pentaerythritol trinitrate):

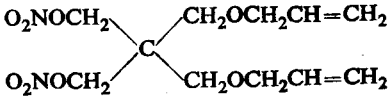


VII

Evans and Gallaghan [55] have nitrated mono- and di-allyl-pentaerythritol to produce trinitrate or dinitrate:



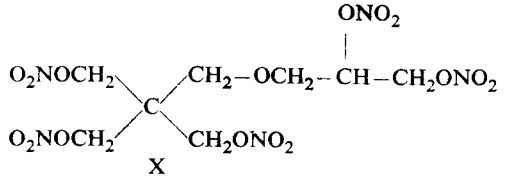
VIII



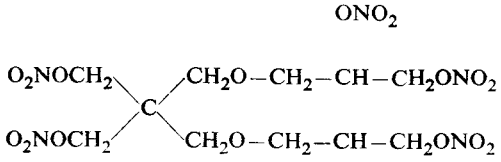
IX

Both these ether-esters are liquids of specific gravity $d_{20}^{20} = 1.373$ and 1.191 respectively.

The same authors succeeded in obtaining glyceryl pentaerythritol ether and diglyceryl pentaerythritol ether, and converted them by nitration into pentanitrate and hexanitrate respectively:



X
(m.p. 55°C)



XI

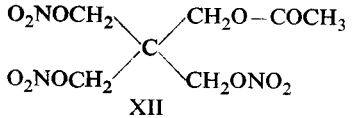
The ether-ester (XI) is an oily liquid, of specific gravity $d_{20}^{20} = 1.540$.

PENTAERYTHRITOL TRINITRATE

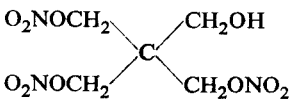
Initially, attempts to introduce fewer nitro groups into a molecule of pentaerythritol by means of direct nitration were unsuccessful. When less concentrated nitric acid was used the only result was a decreased yield of PETN contaminated by small quantity of pentaerythritol trinitrate.

For a long time the only practicable method was the nitration of an organic acid pentaerythritol ester followed by removal of the acyl.

In this way Marans, Elrick and Preckel [52] have obtained pentaerythritol monoacetate together with certain amounts of di- and triacetate by heating pentaerythritol tetra-acetate with pentaerythritol at 180–185°C. The monoacetate was nitrated to yield pentaerythritol acetate trinitrate (XII). Careful hydrolysis of the latter produced pentaerythritol trinitrate (XIII):



XII
m.p. 87–88°C



XIII
m.p. 27–28°C

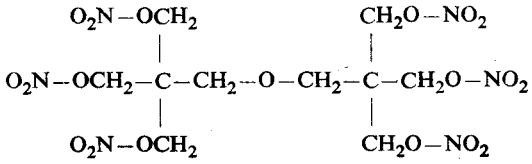
However, it has been discovered that pentaerythritol trinitrate can also be produced by direct nitration of pentaerythritol with a mixed acid composed of 80% nitric acid and 80% sulphuric acid (Camp, Marans, Elrick and Preckel [56]). The nitration is performed at a temperature close to 0°C. The product, representing a mixture of PETN with trinitrate, is precipitated by adding water. To separate the components the acetone solution neutralized by means of ammonium carbonate is treated with aqueous alcohol so as to form a mixture of 7 parts of acetone, 3 parts

of water and 2 parts of ethanol. PETN precipitates from this solution, while pentaerythritol trinitrate remains in the liquor to be completely separated as a precipitate by further treatment with hot water. The yield of trinitrate amounts to about 50%.

Pentaerythritol trinitrate can be used for preparing a range of mixed pentaerythritol esters.

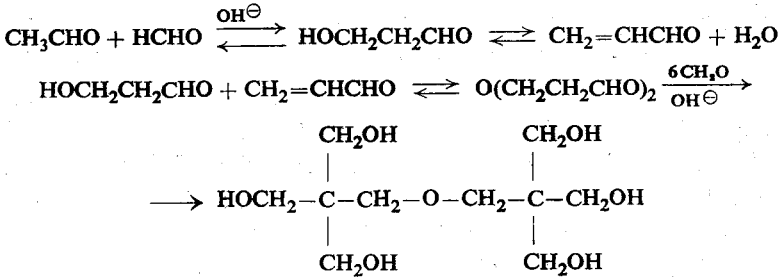
DIPENTAERYTHRITOL HEXANITRATE (NITRODIPENTA, DiPEHN)

DiPEHN melting at 72°C, and the alcohol from which the ester is derived, have been obtained by Friedrich and Brün [6].

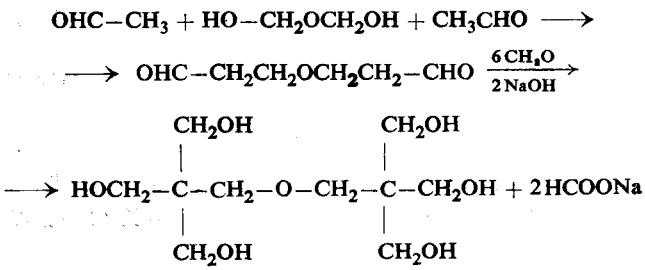


Their work has shown that some dipentaerythritol is always produced alongside pentaerythritol during chemical combination of acetaldehyde and formaldehyde. The proportion of dipentaerythritol formed depends on the conditions under which the reaction of the two aldehydes takes place.

According to Wawzonek and Rees [3] dipentaerythritol is formed as a result of a series of reactions, in which acrolein is one of the intermediates:



Barth, Snow and Wood [4] have proposed another reaction scheme approaching to that outlined by Tollens and Wigand [2], in which they assume that formaldehyde is present in the form of a polyoxymethylene chain:



In order to produce dipenta [6] one equivalent of acetaldehyde is allowed to react with three equivalents of formaldehyde in the presence of half a mole of calcium hydroxide. In that way, pentaerythritol containing about 15% of dipentaerythritol is formed. This mixture melts at 221°C.

The melting point of pure dipentaerythritol is 221–222.5°C. From pentaerythritol and dipentaerythritol a eutectic mixture of 70% pentaerythritol and 30% dipentaerythritol melting at 190°C is formed.

Nitrodipenta resembles PETN in its physical and chemical properties. Nitrodipenta dissolves in acetone more readily than PETN, and this is used to separate the two nitrates. The specific gravity of single crystals of nitrodipenta is 1.630 at 15°C, while pellets prepared under a pressure of 2500 kg/cm^2 acquire a specific gravity of 1.589. Nitrodipenta is less sensitive to impact and to friction than PETN and its temperature of initiation is higher. In spite of this, its chemical stability at 100°C is distinctly less than that of PETN. This is the main reason why the presence of nitrodipenta in PETN is undesirable.

Besides, nitrodipenta is a less effective explosive than PETN. As determined by Brün [38] the rate of detonation is 7410 m/sec for nitrodipenta of specific gravity 1.589, the net expansion in the lead block being 75% as that of PETN.

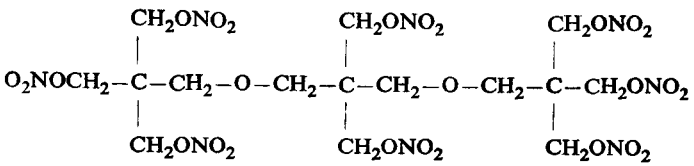
The method of preparing nitrodipenta reported by Friedrich and Brün [6] consists in nitrating pentaerythritol rich in dipentaerythritol and in afterward separating the two components by utilizing their different solubility.

The mixture of alcohols undergoes nitration with nitric acid in the same manner as pentaerythritol, after which the crude product is treated with an equal portion (by weight) of acetone. PETN is insoluble, while nitrodipenta remains in solution with a small quantity of PETN. Water added carefully causes the residual pentaerythritol tetranitrate to precipitate. The solution separates into two layers: the upper composed of fairly hydrated acetone containing a small amount of nitrodipenta, and the lower which consists of a saturated solution of nitrodipenta in acetone containing a little water. The bottom layer is removed and treated with an excess of alcohol. Almost pure dipentaerythritol hexanitrate is precipitated.

It is possible to convert hexanitrate into the original alcohol — dipentaerythritol — by treating its solution in acetone with boiling alkaline sulphide solution in alcohol.

OTHER MIXED ESTERS

Tripentaerythritol octanitrate (Nitrotripenta)

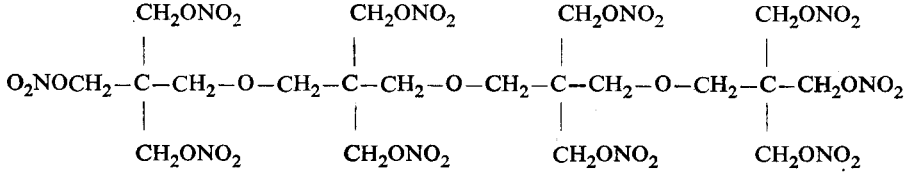


Tripentaerythritol octanitrate (Nitrotripenta) melting at 82–83°C was prepared by Wyler [57] by nitrating tripentaerythritol (m.p. 248–250°C), another by-product of the pentaerythritol reaction.

The formation of tripentaerythritol is favoured by keeping high alkalinity in the pentaerythritol reaction, by using potassium hydroxide or by carrying out the pentaerythritol reaction in the presence of pentaerythritol or dipentaerythritol [58].

Nitrotripenta has been prepared by the nitration of tripentaerythritol with 99% nitric acid at 0–10°C. Nitrotripenta is readily soluble in hot benzene and in acetone, soluble in alcohol and chloroform, insoluble in water. Because of its relatively low melting point, nitrotripenta can be melted and poured, and can therefore be used as a coating agent and sensitizer for ammonium nitrate.

Tetrapentaerythritol decanitrate (Nitrotetrapenta)



Tetrapentaerythritol decanitrate (Nitrotetrapenta) m.p. 70°C was prepared by Wyler [59] by nitrating tetrapentaerythritol (m.p. 234°C).

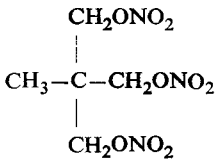
Tetrapentaerythritol was isolated by the same author from technical pentaerythritol by fractional crystallization. It was nitrated with 98% nitric acid at —5 to +5°C. It is readily soluble in acetone and ethylene dichloride. It has been suggested as a coating agent and sensitizer for ammonium nitrate.

Dihydrated pentaerythritol nitrate

Pentaerythritol has been converted to polymeric ethers by the action of heat, preferably in presence of small amounts of acids [60]. Wyler [61] nitrated it and obtained an explosive of the formula $[(C_5H_8)(ONO_2)_2O]_x$, where x has a value between 1 and 7.

1,1,1-Trimethylolethane trinitrate

1,1,1-Trimethylolethane trinitrate (trimethylolmethylmethane trinitrate, nitropentaglycerine, "nitrometriol")



has been proposed by Hertz [62] as an explosive capable of partly or totally replacing nitroglycerine.

Colson [63] has described it as a liquid freezing at —60°C with a specific gravity of 1.4685 at 20°C, and a refractive index of 1.4760 at 17.5°C. Its solubility in water at 19°C is 0.516 g/l. while at 36°C it is 0.685 g/l. According to Médard [64] the melting point of pure nitrometriol is 51°C.

Collodion cotton is readily dissolved by nitrometriol, which in this respect differs from PETN. The heat of explosion is 1270 kcal/kg. The lead block expansion is about 85% that of penthrite and 115% that of picric acid.

According to Médard [64] the rates of detonation developed with non confined nitrometriol cartridges, 30 mm dia., were:

density, g cm^3	1.39	1.48	1.50
rate, m/sec	6750	7040	7060

After being fused the explosive solidifies to form a mass having a density of 1.48 to 1.50 g/cm^3, which needs a very strong initiation by about 30 g PETN to detonate under these conditions with a rate of estimately 6300 m/sec. Being less sensitive to mechanical shock than PETN, methyltrimethylolmethane trinitrate explodes under an impact energy more or less like that needed for tetryl.

Médard has suggested using it in blends with ammonium nitrate (see Vol. III).

During the last war a certain amount was manufactured in Germany for use as a component of smokeless (double-base) powder. The extent of production was limited, however, due to inadequate supplies of propionaldehyde. Trimethylolmethylmethane is produced in an analogous way to pentaerythritol by reacting propionaldehyde with formaldehyde:

$$CH_3CH_2CHO + 3CH_2O \longrightarrow CH_3-C(CH_2OH)_3 + HCOOH$$

Nitrometriol is obtained by nitrating metriol in a manner resembling the production of nitroglycerine.

Colson [63] has reported that as a result of nitrating 100 parts by weight of 1,1,1-trimethylolethane at 10°C by means of a mixed acid containing 45% HNO_3 and 55% H_2SO_4, 197–198 parts by weight of its nitric ester were obtained i.e. about 93% of the theoretical yield. The author considers that it is possible to increase the yield up to 97–98% of theoretical, by using mixed acid fortified with 20% oleum. A continuous method of nitration has also been outlined by Colson: trimethylolmethylmethane was first dissolved in sulphuric acid and then introduced into the nitrating mixture.

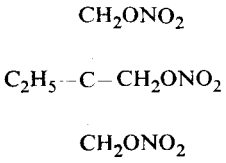
The preparation of mixed trimethylolethane esters, i.e. of acetate–nitrates, was described by Marans and Preckel [65]. By heating metriol in the presence of metriol triacetate at 175–180°C, a mixture of mono- and diacetate is obtained together with unchanged trimethylolethane.

From the nitration of metriol monoacetate metriol acetate–dinitrate is formed as an oily liquid of specific gravity $d^{25} = 1.362$. Cautious hydrolysis of this substance in contact with sodium hydroxide solution in ethanol at room temperature produces trimethylolethane dinitrate with a yield of 75%.

The dinitrate is a liquid, $d^{25} = 1.362$, $n_D^{25} = 1.4692$.

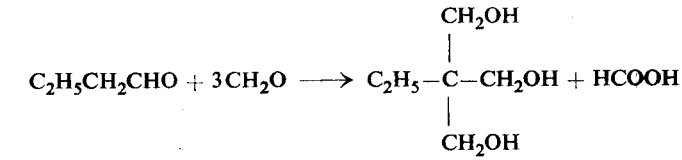
Metriol diacetate can be nitrated to yield trimethylolethane diacetate-nitrate. The latter, subjected to mild hydrolysis, yields metriol mononitrate, a crystalline substance which melts at 76–77°C.

1,1,1-Trimethylolpropane trinitrate (ethyltrimethylolmethane trinitrate)



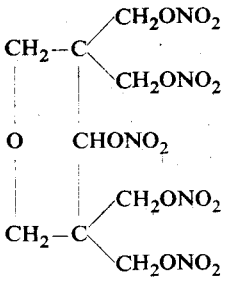
This solid melting at 45°C (Spaeth [66]) is an explosive approaching tetryl in strength. Its sensitiveness to shock lies between that of picric acid and TNT.

To produce the raw material, trimethylolpropane, formaldehyde is condensed with butyraldehyde in an alkaline medium:



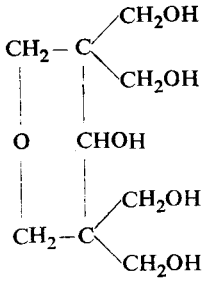
Anhydroenneaheptitol pentanitrate

Anhydroenneaheptitol pentanitrate (3,3,5,5-tetramethylol-4-hydroxypyran pentanitrate) is a derivative of an alcohol called anhydroenneaheptitol produced by esterifying it with nitric acid.



It was first obtained by Hertz [67] who proposed its use as an explosive, since (in the authors opinion) it develops greater explosive strength that PETN but is less sensitive. Tollens and Apel [68] have prepared the initial alcohol (m.p. 156°C) resulting from the reaction of acetone with formaldehyde in the presence of calcium hydroxide, to which they attributed the structure of an enneaheptitol anhydride without, however, determining which hydroxyl groups were dehydrated.

Latter this has been made clear by Mannich and Brose [69] who reported that the pyran ring structure:



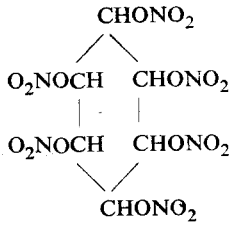
is to be regarded as most probable.

Anhydroenneaheptitol pentanitrate has found no practical application, since the yield of alcohol is low owing to the fact that in the main acetone and formaldehyde react with one another to form polymers of vinyl methyl ketone (methylene acetone) $CH_2{=}CHCOCH_3$ (Müller [70]).

CYCLIC ALCOHOL ESTERS

Inositol hexanitrate

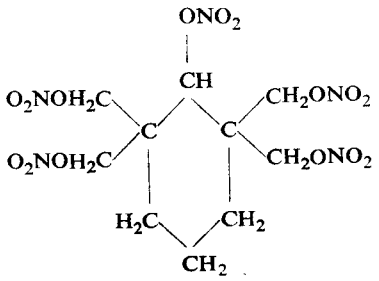
Inositol hexanitrate ("nitroinosite", "nitroinositol"), a solid melting at 132.5°C, and quebrachitol hexanitrate ("nitroquebrachite"), an oily liquid, are esters of isomeric cyclic alcohols. Their common constitutional formula is:



Both esters, and specially hexanitroinositol, were suggested by Crater [71] for use in explosives practice instead of tetryl for filling detonators and boosters. In explosive strength, sensitiveness to mechanical shock, and stability both esters are similar to nitromannite. References to quebrachitol pentanitrate can be found in the patents of Burke and McGill [72].

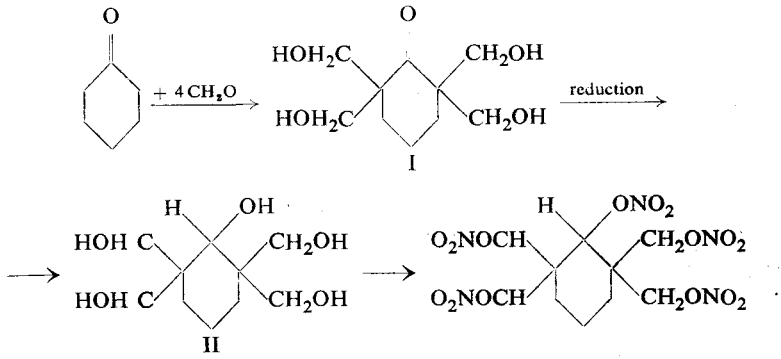
Tetramethylolcyclohexanol pentanitrate

Tetramethylolcyclohexanol pentanitrate ("nitrohexanol") is a solid, melting at 122.5°C



Attention has been drawn to this substance as an explosive by Friedrich and Flick [73]. L. Wöhler und Roth [74] have established its explosive character, determining the heat of explosion to be 900 kcal/kg, $f = 11{,}700$ m and the rate of detonation of a sample of density 1.44 g/cm^3 to be 7670 m/sec.

Nitrohexanol is produced as a result of nitrating the corresponding alcohol (II) obtained from cyclohexanone:

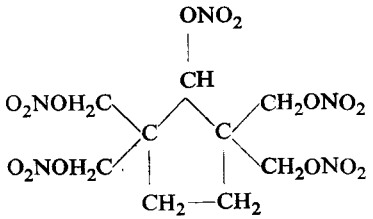


An intermediate product is tetramethylolcyclohexanone (I). Subjected to nitration, this compound yields its tetranitrate ("nitrohexanone") melting at 66°C. The heat of explosion of nitrohexanone is 825 kcal/kg, $f = 12{,}110$ m, rate of detonation being 7740 m/sec at a density of 1.51 g/cm^3.

Up to the present none of these substances are used in practice.

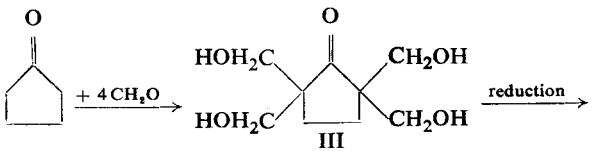
Tetramethylolcyclopentanol tetranitrate

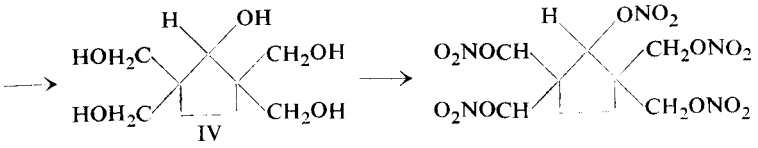
Tetramethylolcyclopentanol tetranitrate ("nitropentanol") is a solid melting at 92°C.



It was first described by Friedrich and Flick [73] and its explosive properties were examined by L. Wöhler and Roth [74]. Nitropentanol is a strong explosive: its heat of explosion is 1035 kcal/kg, the rate of detonation is 7360 m/sec at a density of 1.57 g/cm^3, $f = 12{,}550$ m.

It is obtained by the nitration of an alcohol (IV) obtained from cyclopentanone:





IV

Tetramethylolcyclopentanone (III) is an intermediate product in the above reaction chain. It can be nitrated to give a tetranitrate, m.p. 74°C (nitropentanone). Friedrich and Flick report the explosion heat of nitropentanone as 820 kcal/kg, $f = 10{,}680$ m and the detonation rate 7940 m/sec at a density of 1.59 g/cm^3. These substances are not in practical use at present.

NITROALCOHOL ESTERS

Nitroalcohols are produced when nitroparaffins react with formaldehyde in an alkaline medium (Henry [75]). In the case of primary paraffins, the reaction proceeds as below:

$$R-CH_2NO_2 + 2CH_2O \xrightarrow{OH^\ominus} R-C(CH_2OH)_2-NO_2$$

With nitromethane, a trihydric alcohol, trimethylolnitromethane, so called nitroisobutylglycerine, is formed:

$$CH_3NO_2 + 3CH_2O \longrightarrow HOCH_2-C(CH_2OH)_2-NO_2$$

Trimethylolnitromethane trinitrate

$$O_2N-C(CH_2ONO_2)_3$$

Trimethylolnitromethane trinitrate, known also as nitroisobutylglycerine trinitrate (other names are nitroisobutanetriol trinitrate, NIB-glycerine trinitrate) is an oily liquid, freezing at —39°C (Hofwimmer [76]), but crystallizing only with the greatest difficulty. It is immiscible with water, but soluble in the most of organic solvents except petroleum ether (like nitroglycerine). It is capable of dissolving collodion cotton but not so effectively as nitroglycerine. Its specific gravity is 1.68. The substance is more viscous and less volatile than nitroglycerine.

Opinions about the chemical stability of nitroisobutylglycerine trinitrate do

not agree. Naoúm [31] reported its stability between the temperatures of 70 and 80°C to be the same as that of nitroglycerine. Other sources, on the contrary, report inadequate stability which, however, can be ascribed to the presence of impurities difficult to remove (see further under preparation of the substance).

Trimethylolnitromethane trinitrate has attracted considerable interest as an explosive owing to its ideal oxygen balance. Explosive decomposition results in production of heat exceeding that produced by nitroglycerine by 7%

$$NO_2 \cdot C(CH_2ONO_2)_3 \longrightarrow 4CO_2 + 3H_2O + 2N_2 + 1707 \text{ kcal/kg}$$

Its sensitiveness to impact is of the same order as that of nitroglycerine. The initiation temperature is 180°C.

In the lead block trimethylolnitromethane trinitrate produces an expansion slightly greater than that of nitroglycerine, i.e. 105–110% of the value for nitroglycerine. Blasting gelatine made from nitroisobutylglycerine trinitrate is, in spite of this, somewhat weaker than blasting gelatine from nitroglycerine because nitroglycerine applied as a component of gelatine furnishes it with some oxygen to oxidize the nitrocellulose component of this explosive. Thus, according to Naoúm [31], a 93% blasting gelatine from trimethylolnitromethane trinitrate gave a 580 cm^3 expansion in the lead block, while gelatine from nitroglycerine gave 600 cm^3.

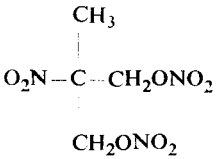
The mode of preparation of nitroisobutylglycerine trinitrate investigated particularly by Aubry [77] consists in nitrating NIB-glycerine with a mixture of nitric and sulphuric acid under conditions more or less approximating to those applied in nitroglycerine manufacture. Being more viscous the nitrated product compares unfavourably with nitroglycerine in that acids are washed out with difficulty. The yield is nearly 90% of theoretical (about 243 parts of nitrate from 100 parts of trimethylolnitromethane).

The quality of the product and especially the effectiveness of water washing are dependent on the purity of the original raw material since the presence of impurities cause the ester to form emulsions with water.

Nitroisobutylglycerine for nitrating purposes should have a melting point not lower than 150°C (the pure compound melts at 164–165°C).

Its practical application depends on the manufacture of nitromethane, which can be now obtained by vapour phase nitration (Hass *et al,* [78]; T. Urbański and Słoń [79]).

Dimethylolnitroethane dinitrate



Dimethylolnitroethane dinitrate (2-nitro-2-methylpropanediol-1,3-dinitrate) is a solid melting at 38°C, of low volatility, dissolving nitrocellulose readily enough.

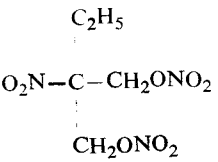
The substance was first described in a report by Bergheim [80] and afterwards by Wyler [81] and Médard [82]. It is an explosive a little weaker than nitroglycerine, but slightly stronger than cyclonite. Its heat of explosion is about 1250 kcal/kg. Its sensitiveness to impact is distinctly less than that of nitroglycerine. Wyler has estimated the sensitiveness to shock as approximately the same as TNT. Médard has reported it to be slightly higher than that of tetryl, and comparable with cyclonite.

When compressed the product can attain the following densities:

under a pressure of 1360 kg/cm^2 $d = 1.58$
under a pressure of 2760 kg/cm^2 $d = 1.61$

Médard has established that the chemical stability of this compound is insufficient for any wider use in explosives technology.

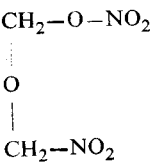
Dimethylolnitropropane dinitrate



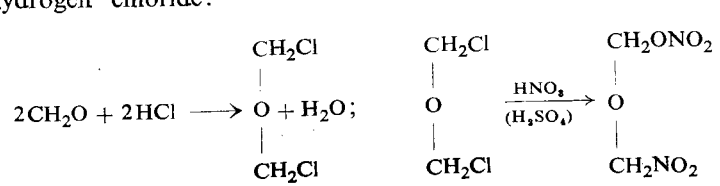
Dimethylolnitropropane dinitrate (2-ethyl-2-nitropropanediol-1,3-dinitrate) is a liquid that does not dissolve nitrocellulose.

Médard [83] found that it is a stronger explosive than picric acid, producing in the lead block an expansion some 25% larger. Its sensitiveness to mechanical shock is appreciably smaller than that of picric acid.

Nitromethoxymethanol nitrate



This ester, known as methyl ether nitronitrate (more correctly as nitromethoxymethanol nitrate), is a colourless, oily liquid, boiling at 48°C at 15 mm Hg with a specific gravity 1.50 at 20°C. It readily dissolves collodion cotton, and is more volatile than nitroglycol. It was first produced by Moreschi [84] by nitrating *sym*-dichlordimethyl ether formed by reacting a 40% formaldehyde solution with gaseous hydrogen chloride:



T. Urbański and Magiera [85] have examined the chemical stability and explosive properties of the ester and conclude that neither the substance itself nor a solution of nitrocellulose in it are sufficiently stable for practical application. Its temperature of initiation is 150°C (whereas nitroglycol is initiated at 220°C), and it is considerably more sensitive to impact than nitroglycol. They also found that an impact energy of 0.91 kgm/cm^2 is necessary to ensure a 10% probability explosion of nitroglycol, as compared with barely 0.11 kgm/cm^2 for the ester.

Nitromethoxy methanol nitrate produced a lead block expansion of 420 cm^3 whereas the net expansion produced by nitroglycol in the same series of experiments was 450 cm^3.

During the reaction between formaldehyde and hydrogen chloride a chloroether is also produced: $ClCH_2OCH_2OCH_2Cl$. According to Houben and Pfankuch [86] nitration of this substance produces a nitronitrate $O_2NOCH_2—O—CH_2OCH_2NO_2$ boiling at a temperature of 88°C under 9 mm Hg. It is less volatile than the other nitronitrate, though more volatile as nitroglycol.

T. Urbański and Magiera have found that this compound had similar explosive properties, low chemical stability, high sensitiveness to shock, and produced a large expansion in the lead block (440 cm^3).

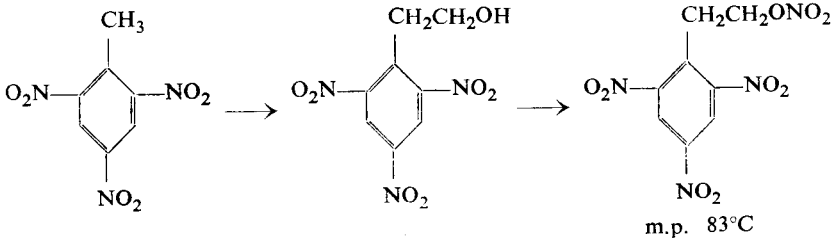
Neither of these substances has been used in practice, owing to their low stability.

NITROAROMATIC ALCOHOL NITRATES

There exists a range of explosives which are prepared by the nitration of aromatic alcohols. None of these explosives has found practical application, though this might be possible providing the costs of production were not too great and the explosive strength sufficiently high. This group of materials includes such compounds as: dinitrobenzyl nitrate [106], trinitrohydroxyethylbenzene nitrate, trinitrophenoxyethyl nitrate and the like.

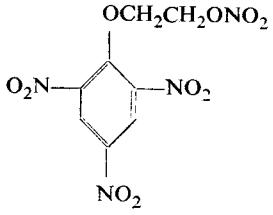
Trinitrohydroxyethylbenzene nitrate

Trinitrohydroxyethylbenzene nitrate or trinitrophenyl-β-ethyl nitrate, melting at 83°C, is obtained from trinitrotoluene, that undergoes an addition reaction with formaldehyde in an alkaline medium to produce the corresponding alcohol (m.p. 112°C), which is then nitrated (Vender [87]):



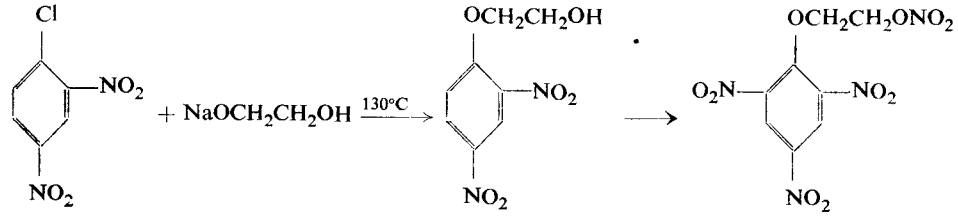
m.p. 83°C

Trinitrophenoxyethyl-ω-nitrate

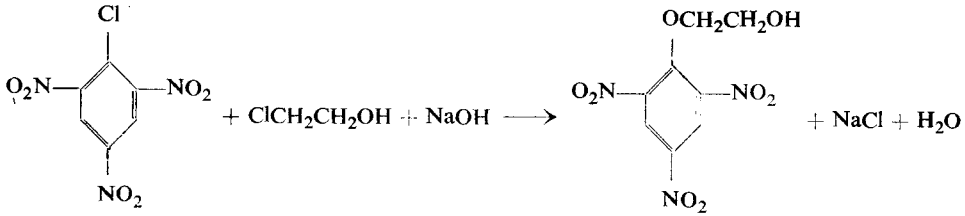


This is a white crystalline powder with a melting point of 104.5°C, soluble in acetone and capable of gelatinizing collodion cotton.

It can be obtained by reacting sodium hydrogen ethylene glyoxide and chlorodinitrobenzene followed by nitration, or chlorotrinitrobenzene, as reported by Faibourne and Toms [88]:

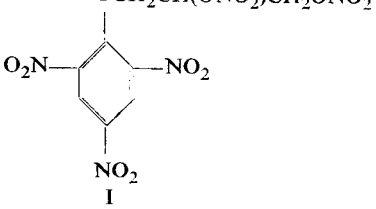


Trinitrophenoxyethyl alcohol, the parent substance of trinitrophenoxyethyl nitrate, was also obtained by Wasmer [89] in another way, namely:



Trinitrophenoxyethyl-ω-nitrate is more sensitive to impact than picric acid and less so than tetryl. Its explosive strength approaches that of tetryl, since it produces an expansion in the lead block of 350–355 cm^3.

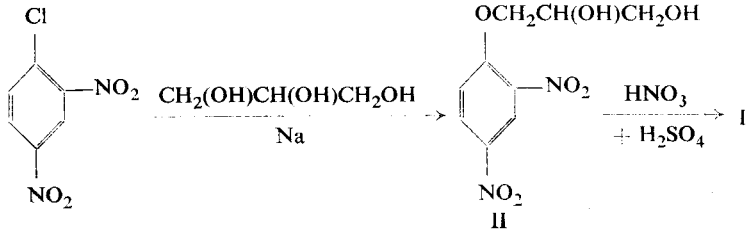
Trinitrophenyl-α-glycerol-β,γ-dinitrate (α-glyceryl-trinitrophenyl ether β,γ-dinitrate)



I

This is a white crystalline substance with a melting point of 125–127°C.

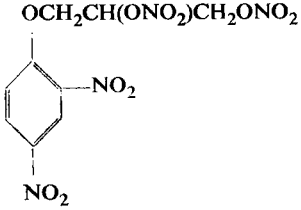
It was suggested as an explosive by Lewis [90] and later described by Desvergnes [91]. According to Willgerodt [92] it is formed by reacting chlorodinitrobenzene with glycerol in the presence of sodium hydroxide to yield dinitrophenyl-α-glycerol (II), followed by nitration:



II

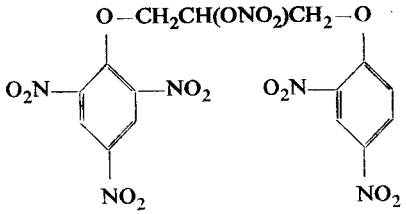
The product (I) gives an expansion in the lead block 25–30% greater than that of picric acid.

The dinitrate of (II) was also obtained [91, 93] as a substance



melting at 119–120°C. See also [94].

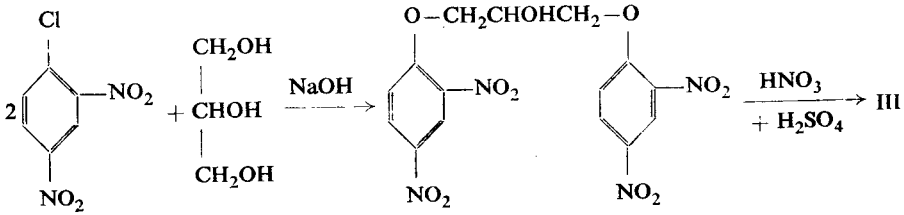
Bis(trinitrophenyl)-α,γ-glycerol-β-nitrate [α,γ-glyceryl-bis(trinitrophenyl)ether] β-nitrate



III

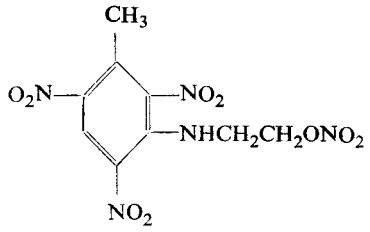
This is a straw yellow crystalline substance with a melting point 178–178.5°C.

It was first obtained and suggested as an explosive by Dynamit A.G. [95]. Later, Desvergnes [91], Stefanović and Ćirić [94] described its preparation by the following sequence of reactions:



(m.p. 173.5–174°C)

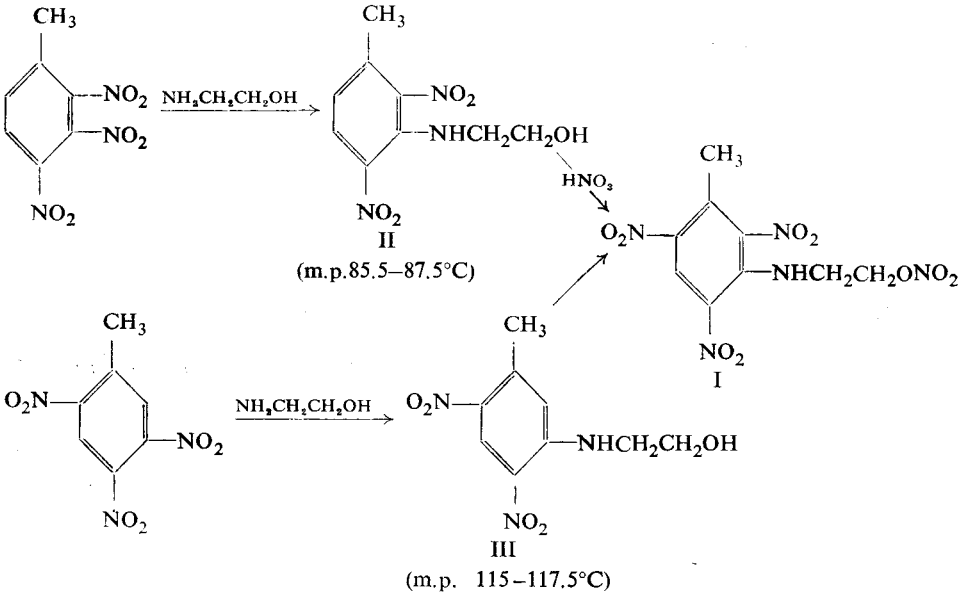
2,4,6,-Trinitro-3-(β-nitroxyethylamine)toluene



I

(m.p. 100–102.5°C)

2,4,6-Trinitro-3-(β-nitroxyethylamine)toluene was prepared by Pluciński [96] as follows:



The compounds (II) and (III) are known in the literature. They were obtained and described by Racciu [97]. Further nitration of both produced (I), according to Pluciński.

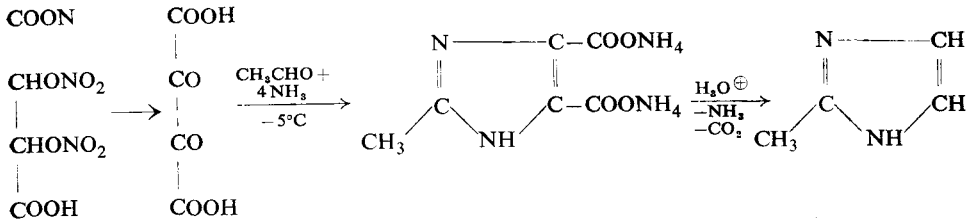
VARIOUS NITRIC ESTERS

Tartaric acid dinitrate

$$COOH{-}CHONO_2{-}CHONO_2{-}COOH$$

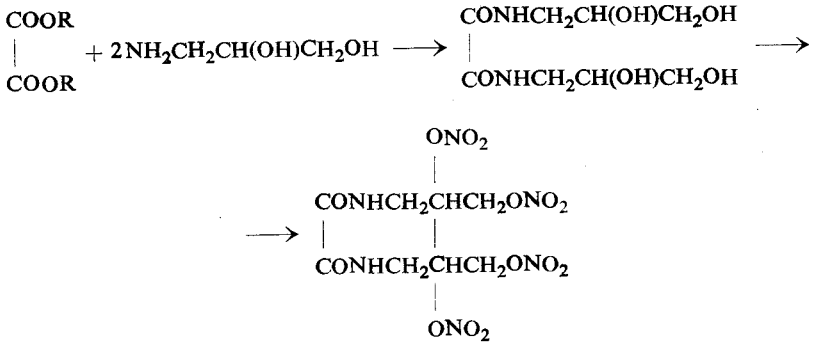
This compound was prepared by Dessaignes in 1857 [98]. The compound is unstable and is spontaneously transformed into dioxosuccinic acid (Kekulé [99], Thiele and Dralle [100] and others [101]).

The high reactivity of the dinitrate may be used to obtain heterocyclic compounds. An ingenious method of forming imidazol derivatives was developed by Payman and Fargher [102]:



Hydroxyalkylacylamide nitrates

Esters of this constitution include: di(hydroxyethyl)-oxamide dinitrate [107] and di-(β,γ-dihydroxypropyl)-oxamide tetranitrate. The latter was first prepared by Domański and Skudrzyk [103] by heating an oxalic acid ester with dihydroxypropylamine to form an amide which was then nitrated, as shown below:



It must be pointed out that experiments intended to attach a nitro group to a nitrogen atom failed. The substance is stable, since it did not undergo decomposition after being maintained for 200 hr at 70°C, and its temperature of initiation is 187°C. Its explosive properties are as follows. At a density of 0.62 g/cm^3 it detonates with a rate of 4030 m/sec, the lead block expansion is 325 cm^3 and its relatively low sensitiveness to shock is indicated by the fact that it is exploded in a drop test by a 2-kg weight falling from a height of 60 cm.

Discussion concerning aminoalcohol esters of nitric acid which are also salts of nitric acid, is developed further in the chapter devoted to nitric salts (see p. 472).

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CHAPTER IX

CELLULOSE AND NITROCELLULOSE

THE most important of the carbohydrate esters of nitric acid are the polysaccharide nitrates, particularly cellulose nitrate or nitrocellulose (NC) and starch nitrate ("nitrostarch") which is much less used. Nitric esters prepared from other sugars such as saccharose and lactose are not of any importance as explosives.

Introduction. Today nitrocellulose is one of most important derivatives of cellulose used in industry and commerce, and a major product of the chemical industry. Its wide and manifold applications are due mainly to its extraordinary physical properties. Thus a protective coating of nitrocellulose varnish, a nitrocellulose film or a tube of smokeless powder — all are characterized by relatively high elasticity and mechanical strength. These properties are a direct consequence of the microstructure of cellulose, which is composed of highly oriented long-chain molecules of polysaccharide. Not only nitrocellulose, but also other derivatives of cellulose, such as other esters and ethers, demonstrate similar characteristics.

Today nitrocellulose is used in the manufacture of all types of smokeless powder, blasting gelatine and dynamites, celluloid, films, varnishes, and artifical leather, in the printing industry and in the pharmaceutical industry.

There exists a range of various kinds of nitrocellulose differing from one another in their physical properties according to the application intended. Nitrocellulose for smokeless powder manufacturing (guncotton) represents one type while other properties are demanded from the raw material to be used for making celluloid or artificial fibres (collodion cotton, collodion nitrocotton).

HISTORICAL

The first reference to the preparation of nitrocellulose was made by Braconnot at Nancy in 1833 [1]. He prepared a number of products he named "xyloidine" by dissolving in nitric acid a series of substances of vegetable origin. The resultant solution was passed into a large amount of water to precipitate xyloidine. Xyloidine obtained in this way was described by the discoverer as a solid, easily inflammable, burning violently and completely to leave no residue. Taking into consideration its mode of preparation, Braconnot's xyloidine probably contained only 5–6% of nitrogen.

Pelouze [2] continued the investigations of Braconnot by subjecting paper or cotton to the action of nitric acid. The difference was that in his experiments the nitrated material was not dissolved in nitric acid, but the product was similar. In later papers it was described under the name of pyroxylin. Extending his earlier researches, Pelouze [3] later established that pyroxylin was a substance differing in principle from the product obtained by nitrating starch.

At the same time some original investigations were described by Schönbein [5] of Basle. In 1845 he began to examine the properties of ozone and "active oxygen". He also investigated how various organic and inorganic substances, among them cotton, sugar etc., behave, when treated with nitric acid in the presence of sulphuric acid. He paid special attention to the properties of the product obtained from cotton which he has named guncotton in order to emphasize the possibility of using it as gunpowder. Indeed, the important contribution of Schönbein was that he indicated the practicability of the large-scale application of nitrocellulose as an explosive.

At the same time Böttger [6] announced the preparation of an explosive cotton in 1846. This was done independently of Schönbein, and Böttger's priority was admitted by Schönbein [5].

Meanwhile Otto [6] had been pursuing the same subject and reported in 1846 that he had succeeded in producing an explosive cotton similar to Schönbein's guncotton by immersing cotton in concentrated nitric acid for about half a minute, followed by washing and drying. Schönbein applied for a patent to protect his method of preparing guncotton. However, when further trials were begun to extend Schönbein's experiments and to develop production on plant scale, serious difficulties arose, mainly due to spotaneous decomposition of the nitrocellulose brought about by the low chemical stability of the product. Thus an explosion took place in 1847 in the nitrocellulose factory of Messrs John Hall and Sons at Faversham, Great Britain, which used the method based on Schönbein's patent [5]. The whole plant was destroyed. In 1848 in France storage buildings containing guncotton suffered a similar misfortune [7] and later an explosion occurred in an Austrian plant where nitrocotton manufacture had been established since 1853 by Lenk von Wolfsburg [8]. The Austrian authorities viewed the incidence of these explosions in guncotton stores with such anxiety that an edict was promulgated forbidding the manufacture of this product in Austria until its properties were thoroughly understood and production techniques firmly established.

It is now clear that the process of stabilizing nitrocellulose used by Lenk [9] that consisted in washing nitrocellulose with running water for 14 days, followed by a boil with dilute carbonate solution and a final washing with a sodium silicate solution (p. 293), was not sufficient to produce a completely stable product.

Abel takes the credit for explaining that the accidents with nitrocellulose occurred as the result of incomplete removal of readily decomposable products, i.e. they were due to inadequate purification ("stabilization") of the guncotton.

Prolonged boiling of the guncotton with water followed by pulping the substance was introduced by Abel [10]. This technique permitted the removal of the unstable

products from inside the fibres. In this way Abel prepared guncotton which was chemically stable.

At that time, however, the practical application of guncotton was still limited and for a long time attempts to use it as an explosive failed.

A considerable advance in the application of guncotton for military purposes was made when Abel and Brown [11] suggested using a compressed product as a high explosive. The detonation of guncotton was brought about by means of a recently discovered detonator filled with mercury fulminate. The compressed guncotton was intended for the manufacture of demolition charges and for filling mines and torpedoes.

Another appreciable advance was the use of moist guncotton which was safer to handle. Detonation was achieved by means of a gaine (booster) made from dry guncotton initiated by a detonator.

For a time compressed guncotton was used in Russia by the artillery (1876) [12] as a shell filling. From 1890 moist guncotton was adopted for this purpose [12]. Guncotton continued to be used for a shell filling in some countries until it was replaced by the introduction of picric acid.

However, the widest military application for nitrocellulose was in the manufacture of smokeless propellants, which will be discussed in more detail in Vol. III. Between 1891 and 1895 Mendeleyev [13] sought to develop a high nitrated nitrocellulose which would dissolve in the solvent used in smokeless powder manufacture, i.e. in a mixture of alcohol and ether. Earlier work suggested that an increase in nitrogen content would cause the solubility of nitrocellulose to decrease. However, by applying suitable conditions for the nitrating process Mendeleyev prepared nitrocellulose soluble in the ether–alcohol solution despite its high nitrogen content of 12.6%. This be named pyrocollodion cotton or "pyrocellulose".

GENERAL CHARACTERISTICS OF CELLULOSE

Cellulose is one of the most widely distributed natural polymers, since it is one of the principal components of vegetable tissue. It always occurs in nature in the form of fibres varying from the knap-like fibres covering cotton seeds, to the woody substance of trees. The name cellulose is used both for cellulose isolated from the plant, and thus a chemical compound, and for cellulose *in situ* in the form normally occurring in the plant. In the second case cellulose together with hemicelluloses and lignin form the main constituents of the plant.

Little is known of the manner in which these three main components of plant tissue are bound together, whether by purely physical forces or partly by these and partly by chemical links, possibly of the ester type (Hirst [14]).

It is possible, therefore, that isolated cellulose contains some functional groups which were engaged originally in forming the linkages between cellulose and the other components of the plant. Further the isolation of cellulose inevitably causes

some breakage in the long-chain molecule of cellulose, so that in general the average molecular weight of isolated cellulose is lesser than that of cellulose existing in plants. During separation and purification, cellulose oxidation reactions may occur with the formation of new functional groups in the cellulose.

Strictly speaking it is possible to isolate cellulose from any plant. However, in the selection of cellulose as raw material for industrial purposes a complex of factors is to be considered:

(a) the cellulose content in the plant, hence the yield of cellulose and the costs of isolating it;
(b) the physical and chemical properties of the cellulose and partly the characteristics of associated substances;
(c) the purpose for which the cellulose is to be used: as a textile, or in the chemical industry.

As a raw material for large-scale nitration, cellulose from cotton, alfalfa and wood pulp is used. Cellulose from annual or biennial plants such as nettle or cereals (straw pulp) etc. is seldom used.

STRUCTURE OF CELLULOSE

Cellulose can be regarded as a polymer of glucose formed by condensation through removal of water molecules. It may well be that cellulose, and also other polysaccharides, are synthesized from glucose in plants according to the equation:

$$n C_6H_{12}O_6 \longrightarrow (C_6H_{10}O_5)_n + n H_2O \qquad (1)$$

This hypothesis is based mainly on the results of hydrolysis, in which glucose is the only product. In contact with dilute sulphuric acid cellulose is broken down as follows:

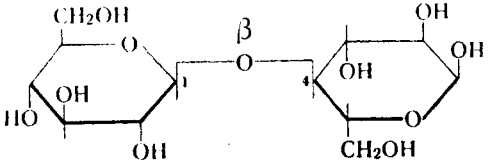
$$(C_6H_{10}O_5)_n + n H_2O \longrightarrow \underset{\text{D-Glucose}}{n C_6H_6O_{12}} \qquad (2)$$

The yield of this reaction may approach the theoretical value (about 96%).

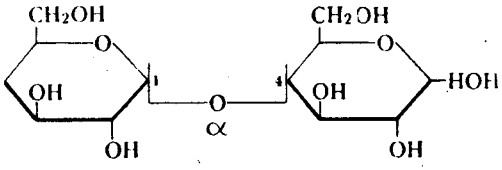
For a long time the degree of polymerization n, of the anhydroglucose units $C_6H_{10}O_5$ remained unknown. Cellulose is insoluble in all common solvents so that it was impossible to estimate its molecular weight by the usual methods, e.g. ebulliometric, cryometric, osmotic and the like. On the other hand, attempts to determine how the molecules of glucose are combined to form cellulose succeeded. As the result of treating cellulose with conc. sulphuric acid in the presence of acetic anhydride, to acetylate the hydroxyl groups and thus protect the compound against more extensive hydrolysis or breakdown, cellobiose acetate was formed. Cellodextrine acetate, composed of a few glucose units can also be formed as an intermediate product. Cellobiose acetate is a derivative of one of the bioses having the general formula $C_{12}H_{22}O_{11}$. Further hydrolysis of cellobiose results in the formation of

D-glucose. This reaction demonstrates the basic difference between the structure of starch and that of cellulose. Starch, in contact with an enzyme amylase (diastase), is broken down to form a different biose maltose, which when hydrolysed in the presence of acid is also converted into D-glucose.

The constitution of both of these bioses has been established by Haworth *et al.* [15]. It was found that the compounds differed from one another in the spacial configuration of the oxygen bond (glucosidic bond): this linkage joins the carbon atoms 1 and 4 which occupy the β-position in cellobiose, and the α-position in maltose:



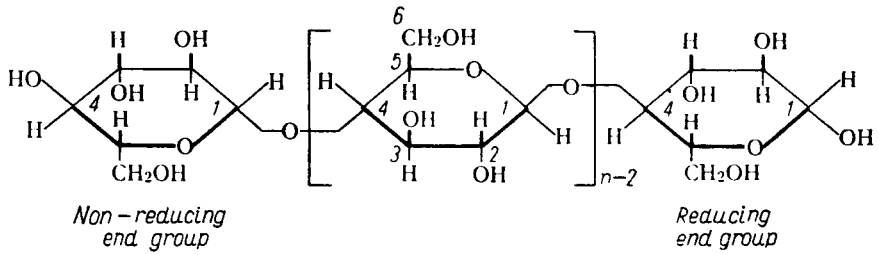
Cellobiose



Maltose

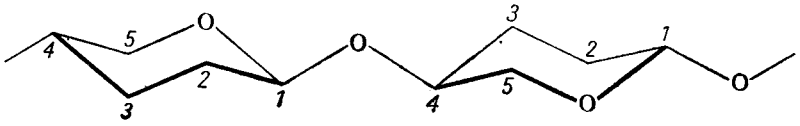
Like all carbohydrates, cellulose possesses the clearly marked prominent properties of an alcohol owing to the presence of hydroxyl (alcoholic) groups. The presence of those groups explains the ability of cellulose to form esters with nitric acid and with acetic acid which have attained great practical importance, and also with sulphuric, phosphoric and different organic acids, as well as the formation of cellulose ethers.

Formation of cellulose ethers and esters has shown that for every six carbon atoms contained in one $C_6H_{10}O_5$ group there are three free hydroxyl groups capable of undergoing esterification or forming ethers. It has also been established that the copper salts of Fehling's solution are reduced by cellulose only to a small extent. Those facts, supported by a series of studies devoted to the products of uncomplete hydrolysis of cellulose, for instance the isolation of cellotriose (Haworth, Hirst and H. A. Thomas [16]), provide sufficient evidence that a molecule of cellulose



is a straight chain composed of glucopyranose rings joined through an oxygen linkage which binds the 1- and 4-carbon atoms in the β-position (the formula is quoted from Sookne and Harris [16a]).

This formula is now regarded as a conventional one, as it is well known that non-aromatic rings of the cyclohexane type, including pyran rings, are non planar strainless rings. According to the present state of the conformation analysis a chair-form is usually attributed to the six membered rings. It follows that the anhydro-glucose units form a chain, a fragment of which consisting of two rings is illustrated below. The glucoside C—O linkages joining the rings are in equatorial conformation.



The terminal glucopyranose rings of the chain contain four hydroxyl groups (two end rings of this type are shown in the formula), so that the hydrolysis of methylated cellulose would be expected to give a certain amount of tetramethylglucose together with a large amount of trimethylglucose. Among the products of hydrolysis 0.6% of tetramethylglucose has indeed been detected, resulting without question from the terminal glucopyranose nuclei, and this enabled Haworth [17] to make the first estimate of the magnitude of a cellulose molecule. He suggested that the molecule contains to some 100–200 anhydroglucose units, which would correspond with a molecular weight of 20,000–40,000.

Other methods of determining the molecular weight of cellulose include the reduction of Fehling's solution (a property of the extreme glucopyranose ring with a hemiacetal group), measurement of the viscosity of cellulose in cuprammonium solution, and estimation of the osmotic pressure of this solution or its sedimentation rate in the ultracentrifuge. The average molecular weight determined by the last three methods was higher than Haworth's original figure, namely 100,000–2,000,000.

Some data for the molecular weight of cellulose of various origins determined by ultra-centrifuging cuprammonium solution, are given in Table 35.

TABLE 35

Origin of cellulose	Molecular weight	Degree of polymerization	Author
Unbleached cotton	1,500,000	9200	Gralen and Svedberg [18]
Purified linters	1,500,000–500,000	10,000–3000	Kraemer [19]
Nettle fibre	1,760,000	10,800	
Ramie fibre	1,840,000	11,300	Gralen and Svedberg [18]
Sulphite pulp	400,000	2900	

According to Bryde and Rånby [20] the degree of polymerization of sulphite pulp varies from 845 to about 3200.

The constitutional formula and molecular weight of cellulose determined on the basis of chemical and physico-chemical experiments has been confirmed by X-ray analysis, which has also led to the discovery of the microcrystalline structure of cellulose. Today the structural model proposed by Meyer and Mark [21] and Mark and Misch [22] based on the X-ray measurements of Polanyi [23] and Sponsler and Dore [24] and taking into consideration Haworth's conclusions about the existence

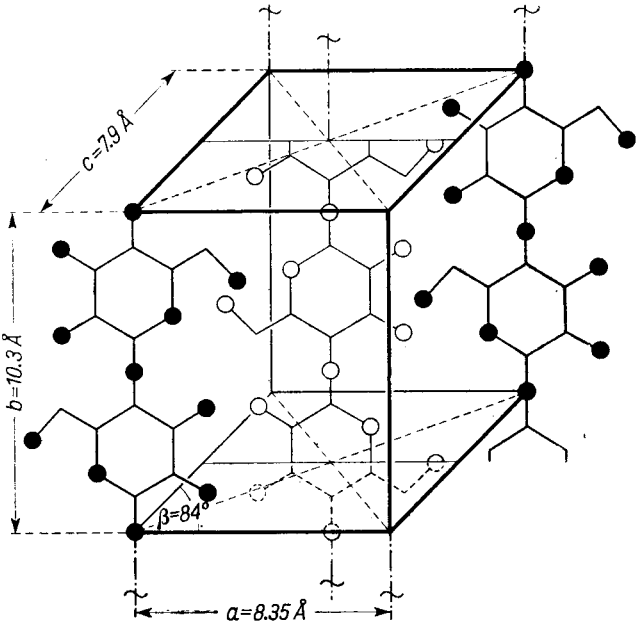


FIG. 75. Unit cell of cellulose I according to Meyer and Mark [21], Mark and Misch [22].

of the bond 1–4 in cellulose, is fully accepted. The fundamental unit of cellulose, in crystallographic measurements, consists of five cellobiose members ranged axially along the cellulose fibre. The dimensions of this unit are as follows: $a = 8.35$ Å, $b = 10.3$ Å (along the fibre axis), $c = 7.9$ Å, the angle β formed by the axes c and a being 84°. A diagram of the crystal unit is given in Fig. 75 in which three of the five cellobiose units are shown.

According to Trommel [24a] the cell dimensions of cellulose are: $a = 8.29$Å, $b = 10.5$ Å, $c = 7.93$ Å, $\beta = 84°53'$. The angle β changes to 90° in the course of the nitration.

Crystalline cellulose is believed to exist in at least four crystalline variations. Cellulose I occurs in the majority of plants. Its crystal structure conforms with the diagram in Fig. 75.

Cellulose II represents cellulose precipitated from solution or regenerated from

an addition compound, for instance alkalicellulose. The essential characteristic of the microcrystalline constitution of cellulose II is a certain deformation of its crystal lattice resulting in a distortion of the β-angle, making it approximately 62° (Andress [25]).

Swelling cellulose I by means of liquid ammonia and precipitating the substance leads to the formation of cellulose III, which also differs from I by virtue of its deformed crystal lattice, in which the β-angle is approximately 58° (Legrand [26].

Regenerated cellulose (cellulose II) heated in water under pressure or in glycerine to 140–300°C yields cellulose IV giving an X-ray picture approximately the same as that of cellulose I, but with a wider β-angle of 90° (Kubo [27]).

The differences in the microcrystalline structure of the different forms of cellulose are compared in Table 36.

TABLE 36

Parameter	Cellulose I	Cellulose II	Cellulose III	Cellulose IV
Axis *a*	8.35 Å	8.1 Å	7.74 Å	8.11 Å
Axis *b*	10.3 Å	10.3 Å	10.3 Å	10.3 Å
Axis *c*	7.9 Å	9.1 Å	9.9 Å	7.9 Å
Angle β	84°	62°	58°	90°

To account for the phenomenon of chelation by intermolecular hydrogen bonds, Pierce [28] has suggested an alternative constitution for cellulose, as shown in Fig. 76.

Carbon atoms are depicted as single circlets, the oxygen atoms of the primary alcohol groups as two concentric circlets, the oxygen atoms of the secondary hydroxyl groups as two concentric circlets, the inner one being marked with a broken line, and the hydrogen bonds are indicated by the letter H.

A similar system has also been proposed by Hermans [29] who postulated that the hydroxyl groups at the carbon atoms 3 and 6 were capable of forming hydrogen bonds with neighbouring oxygen atoms. The existence of hydrogen bridges in cellulose has been demonstrated by analysing its infra-red spectrum and the spectra of its derivatives (Nikitin [30], Konkin *et al.* [30a]). This is discussed on p. 287.

The existence of hydrogen bonds joining the straight chains of cellulose explains the rigidity and mechanical strength of cellulose fibres.

Cellulose fibres are probably packed parallel to one another lengthwise along the axis to form bundles, so called micelles, which are highly oriented along the fibre axis, thus giving cellulose its characteristic mechanical properties.

On the basis of X-ray measurements it is assumed that a micelle composed of 100–170 simple cellulose chains has a length of at least 600Å and a width of 50–60Å. An outline of the micellar structure of cellulose, according to Meyer and Mark [31], is sketched in Fig. 77. The "secondary" valencies (*a*) unite individual

chain-molecules while the "tertiary" valencies (*b*) join different micelles in a given system. The micellar theory of the structure of fibrous substances was suggested as early as 1858 by the Hungarian botanist Nägeli [32] while taking into consideration the double refraction of light by fibre-like substances. He published the hypothesis that substances showing a fibrous texture under the microscope were com-

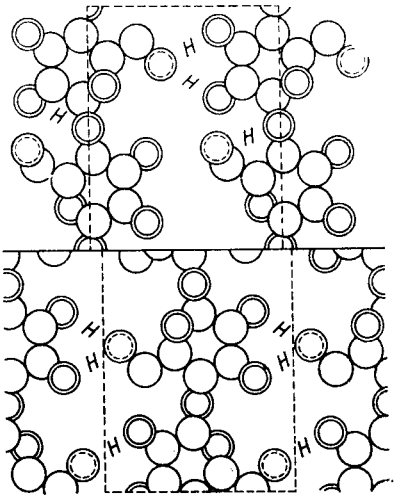


FIG. 76. Diagram of the structure of native cellulose with hydrogen bonds according to Pierce [28].

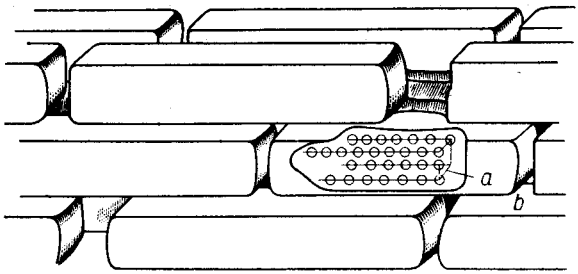


FIG. 77. Diagram of the micellar structure of cellulose according to Meyer and Mark [31].

posed of smaller units, invisible under the microscope, that were also fibre-shaped particles. This theory, once forgotten, has been revived as the result of more modern studies with fibrous substances.

The views of Mark and Meyer have been modified and extended by several authors, e.g. Katz [33], Rogovin [34], Kargin [35] and others [36]. The most serious objections to the Mark and Meyer's theory are: (1) the hypothesis cannot explain the process of swelling, for it does not show why micelles are not destroyed when a liquid penetrates into the fibre; (2) Staudinger's investigations on

viscosity shown that cellulose micelles possess a length of the order of some 10,000 Å, a value distinct greater than that of 600 Å as estimated by X-ray experiments. An alternative concept of micellar structure emerged from this discussion, formulated by Frey-Wyssling [37], Kratky [38] and Rogovin [34]. Mark [39] and Meyer [40] accepted it and it is now generally known as the "fringe micellar theory".

According to this theory the micelles are considered as statistically distributed regions of ordered lattice, consisting of approximately parallel chain "crystalline"

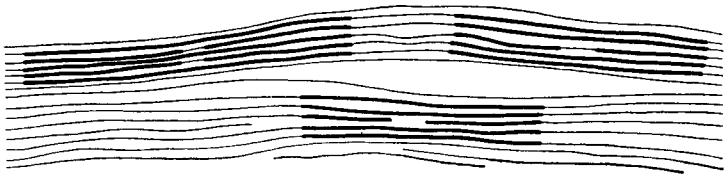


FIG. 78. Diagram of the micellar structure of cellulose according to Rogovin [34].

molecules in an "amorphous" mass. Generally speaking, cellulose fibre is a two-phase system, wherein the crystalline substance is one phase, and amorphous cellulose the other. The characteristic feature of the micellar theory of cellulose proposed by Rogovin [34] is that the term "micelle" is to be understood as an aggregation of highly oriented cellulose chains (Fig. 78) which are situated very close to one from other, hence the energy of the bonds joining the chain-molecules is high. Such aggregations are situated in a complex of non-oriented amorphous chains.

Non-oriented chains are indicated in the diagram by thin lines, while micelles, that is oriented parts, are marked with thicker ones. This concept made many facts explicable. Thus the spectrum of cellulose with about half its hydroxyl groups esterified with nitric or acetic acid showed an unchanged fibrous structure (Hess and Trogus [41]). To explain this, Rogovin suggests that the esterification proceeds in the non-oriented cellulose so that in effect the spectrum of the micelles remains unchanged. In the same way the swelling of cellulose fibres takes place in the amorphous phase, the micelles remaining as well oriented as before and therefore giving the distinctive X-ray diagram of the fibrous structure.

A similar theory was published by Frey-Wyssling [37] who suggested a scheme composed of two projections outlined in Fig. 79, where the crystalline phases of the cellulose fibre are marked as dotted line rectangles.

The spatial configurations proposed by Kratky [38] and Mark [39] repeat in principle the basic idea of the fringe micellar theory, according to which long cellulose chains lie lengthwise through the crystal and amorphous phases form the fibre (Fig. 80).

The letters a, a', b', represent the ends of molecules in the crystal phase of the micelle, b, the ends of molecules in the non-crystalline phase, l the length of the crystalline phase.

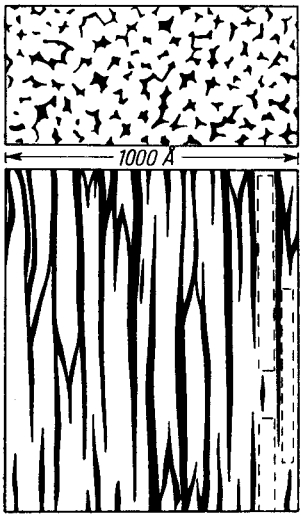


FIG. 79. Diagram of the micellar structure of cellulose according to Frey-Wyssling [37].

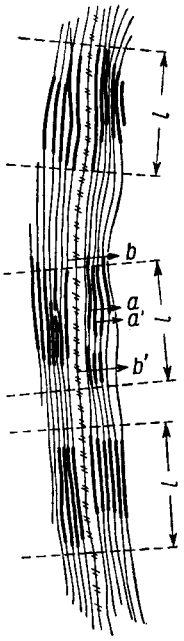


FIG. 80. Diagram of the fringe micellar structure according to Mark [39].

Figure 81 is an electron micrograph of section of cellulose fibre, enlarged 39,000 times. The micellar texture of the fibre is clearly visible.

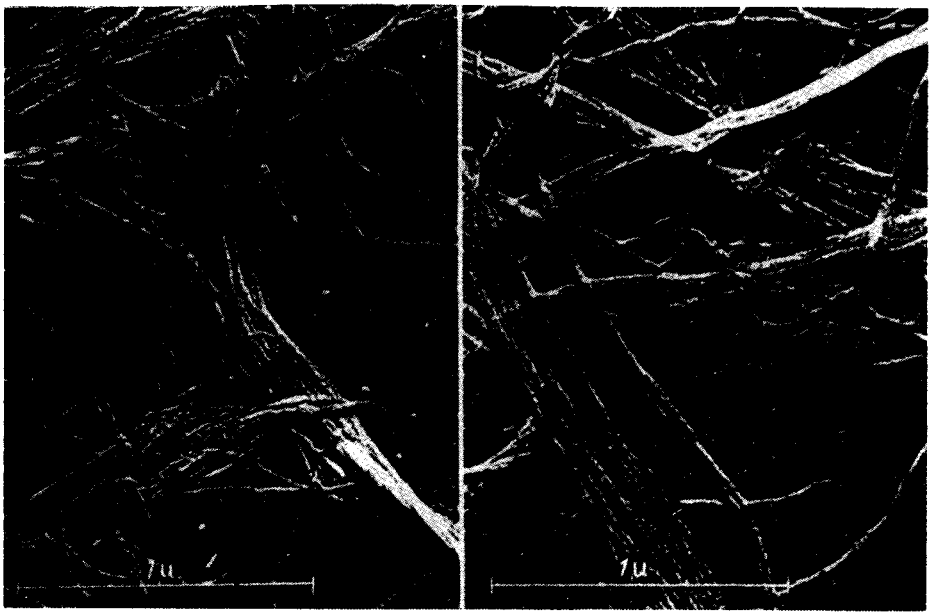


FIG. 81. Electron micrograph of cellulose fibres, from purified cotton and wood pulp respectively, magnification 39,000, according to Rånby [41a].

The Soviet authors Kargin *et al.* [35, 42] and Kozlov [43] have developed the theory of fully amorphous cellulose. Kargin and Leipunskaya [44] have drawn similar conclusions from an electron diffraction study of cellulose esters, including nitrocellulose.

At the present moment it is difficult to decide which of the two hypotheses concerning the structure of cellulose is correct: the idea of an amorpho-crystalline structure, or that postulating solely an amorphous texture. Nikitin assumes that the first hypothesis is the more probable, more especially as it is well in line with the most recent work of Zaydes and Sinitskaya [45] who conclude on the basis of electron diffraction investigations that in the natural cellulose fibre of Chinese nettle, there exist phases having a distinct microcrystalline structure. This suggests that structures shown in Figs. 78, 79 and 80 are the most probable.

Further evidence in favour of the amorpho-crystalline texture was recently provided by Rånby [46]. In a series of his papers several questions connected with the microstructure of cellulose are made clear. Cellulose to be examined in an electron microscope was initially dispersed by means of ultrasonic waves. In this way Rånby has isolated elementary thread-like micelles of about 70 Å dia. Any dimension characterizing the length of the micelle is however missing.

From an examination of α-, β-, and γ-cellulose of spruce (the classification of cellulose in α-, β-, and γ-variations is described in more detail on p. 230) Rånby arrived at the idea that the α-fraction consisted to thread-like micelles 80 Å dia. β-Cellulose has a similar structure, but with shorter micelles and seems

likely to be a degraded form of α-cellulose. γ-Cellulose, however, is amorphous and contains no thread-like micelles. It appears to be composed of different polyoses including hemicelluloses together with amorphous cellulose filling the space between the micelles.

Cellulose dissolved in Schweitzer's reagent (cuprammonium) demonstrates strong laevo-rotatory optical activity. The optical activity of cellulose solutions differing in origin and of different morphological structure is the same.

CHEMICAL PROPERTIES OF CELLULOSE

Wetting and swelling. As stated above, the presence of hydroxyl groups in cellulose enables it to be esterified up to a maximum of three ester groups to every anhydroglucose unit. Further, the high content of hydroxyl groups endows cellulose with hydrophilic properties. Nevertheless, the amount of water absorbed by cellu-

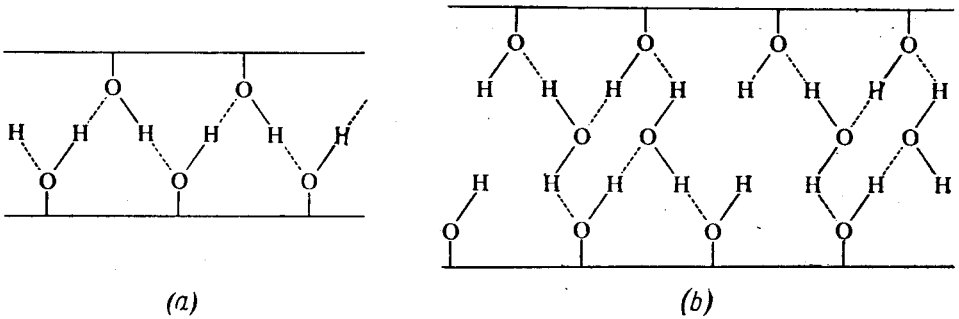


FIG. 82. Chains dry (a) and wet—swollen (b) cellulose with hydrogen bonds.

lose from an atmosphere saturated with moisture is smaller than would be expected for a substance containing so many hydroxyl groups. The maximum quantity of water taken up by cellulose is 16%. Esters of cellulose are appreciably less hygroscopic. Their hygroscopicity decreases as the number of ester groups increases though esterification does not totally eliminate hygroscopicity.

The affinity of cellulose and its derivatives for water can be explained by the existence of hydrogen bonds that bind the molecules of the cellulose chain either directly or with the help of water molecules, as outlined in Fig. 82. The existence of hydrogen bonds has been confirmed experimentally by studies of the infra-red absorption spectra of cellulose and its derivatives (the subject will be discussed later, on p. 287).

Moreover the presence of chelate bonds makes it possible to explain both certain properties of nitrocellulose and phenomena connected with the esterification reaction mechanism of cellulose, all of which will be discussed later.

According to Mark [39] the anhydroglucose units are combined along the *a*-axis (Fig. 75) by means of linkages, the energy of which amounts to *ca.* 50 kcal/mole.

The energy of hydrogen bonds is 15 kcal/mole, while that of the intermolecular (van der Waals) bond acting mainly in the direction of *c*-axis corresponds to 8 kcal/mole.

Another typical property of cellulose and its derivatives dependent on water sorption is the swelling of the fibre that occurs under the influence of certain solutions such as aqueous sodium hydroxide or an ammoniacal solution of cupric oxide, i.e. "cuprammonium". The process of swelling does not start with sorption as in the instance of water. In the first stage of swelling the liquid penetrates the molecular chains of the cellulose, gradually coming in contact with all of them so that chemical combination takes place to form alkali celluloses, $(C_6H_{10}O_5)\cdot NaOH$ and $(C_6H_{10}O_5)_2\cdot NaOH$.

Compounds of this type are unstable, and hydrolyse in water, hence sodium hydroxide can be completely removed by water washing. In effect swollen cellulose is produced. Formerly, in view of the difficulty of removing the water contained in such cellulose by drying, it was called hydrated cellulose, the idea that it represented a water-cellulose compound, a "cellulose hydrate", being current at that time.

Cellulose hydrate is more hygroscopic than cellulose and demonstrates increased reactivity, e.g. esterification. Cellulose hydrate can also be produced by the action of dilute nitric acid.

In certain cases as for instance by treatment of cellulose with cuprammonium, swelling virtually dissolves the cellulose. (The theory of swelling and solution of nitrocellulose is developed in more detail on p. 244). During swelling a characteristic increase in the diameter of the fibre occurs, without any increase in its length.

Sorption and swelling are accompanied by the evolution of heat (Katz [33]). Water sorption causes the evolution of some 3.5–6.0 kcal/mole. The heat of swelling in the presence of sodium hydroxide depends on its concentration. When a 5–18% sodium hydroxide solution is used, the heat of swelling amounts to 13–30 cal/g of cellulose.

Degradation of cellulose. In contact with hydrolysing or oxydizing agents, cellulose undergoes hydrolysis, or oxidation accompanied by hydrolysis, to form hydrocellulose or oxycellulose.

Hydrocellulose is formed when pure cellulose is subjected to the action of cold mineral acids solutions. Hydrolysis then proceeds by stages to yield glucose as the final product. It is possible to stop the hydrolysis at any desired moment, for example by diluting the reaction mixture with water. Hydrocellulose then remains in the form of non dissolved fibres or as powder (Girard [47]). The hydrolysis is usually performed by means of hydrochloric acid or with hydrogen chloride in an anhydrous medium. In the latter case, a water-soluble addition compound $(C_6H_{10}O_5)_2.3HCl$ may occur as a transient product, as reported by Hess and M. Ullman [48].

The changes that occur when cellulose is subjected to hydrolysis all follow from the destruction of the 1,4-glucoside bond. Thus the cellulose chains are shortened and a decrease in the average molecular weight takes place and the cellulose fibres

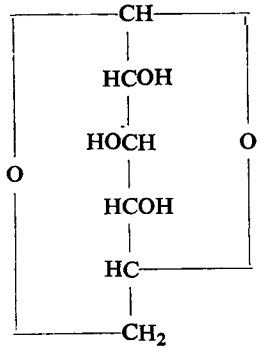
lose some of their tensile strenght and elasticity. Hydrocellulose can reduce Fehling's solution, a property that accords well with the presence of hemi-acetal groups at the terminal anhydroglucose rings.

Hydrocellulose is partially soluble in sodium hydroxide solution. The stronger the reducing action of the hydrocellulose the better its solubility, which can vary from 2–10% in a solution containing 18% NaOH, at room temperature. At a low temperature, e.g. —5°C, the solubility is higher.

Oxycellulose is formed by the action of oxidizing agents such as hypochlorite solutions, hydrogen peroxide and atmospheric oxygen, acting in the presence of a sodium hydroxide solution. The properties of oxycellulose depend on its method of preparation. Oxidation in a neutral or acid medium gives a product with definite reducing properties, indicating the presence of aldehyde groups. Oxidation in an alkaline medium gives a product with acidic properties, indicating the presence of carboxylic groups. An oxycellulose of this kind is distinguished from the other by its capacity of being coloured by methylene blue.

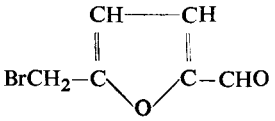
Sodium hydroxide solution partially dissolves oxycellulose. The remaining insoluble fraction does not possess reducing properties. The tensile strength of oxycellulose fibres is lower than that of cellulose fibres, but depending on the mode of preparation they may possess a higher strength than hydrocellulose fibres.

Effect of other factors on cellulose. Dry distillation at a temperature above 150°C causes cellulose to produce compounds of low molecular weight, such as water, methane, ethylene, carbon monoxide, carbon dioxide, acetic acid, and acetone. According to Pictet [49] dry distillation under reduced pressure yields a substance having the empirical formula $C_6H_{10}O_5$, laevo-glucosan which probably is β-D-glucopyranose anhydride:



Later on the decomposition of cellulose at high temperature was examined by a number of authors. Most of the research was devoted to the problem of the origin of coal. The experiments of T. Urbański *at al.* [50] using infra-red spectroscopic analysis for the examination of the products of thermal decomposition of cellulose are described in Vol. III. (Charcoal for blackpowder manufacture).

Cellulose brought into contact with hydrogen bromide is converted in ω-bromomethylfurfural



Cellulose can be degraded by different bacteria. One type of micro-organism causes a methane fermentation, which yields methane, carbon dioxide and lower fatty acids. A hydrogen fermentation is possible, giving H_2, CO_2 and the same acids. There is also a methane–hydrogen fermentation and nitrogen fixing bacteria which assimilate nitrogen from the atmosphere can bring about a breakdown involving the formation of nitrates. In the presence of the nitrates synthesized by these bacteria, cellulose is decomposed with evolution of nitrogen.

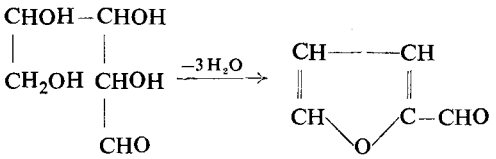
The decomposition of cellulose can be also brought about by moulds, usually by moulds such as *Aspergillus* and *Monilia*. The process is one of slow decay. Others however, for instance *Merilius domesticus*, decompose wood cellulose very quickly.

SUBSTANCES ACCOMPANYING CELLULOSE

In addition to cellulose certain related substances, namely hemicelluloses and lignin, occur widely in plants.

HEMICELLULOSES

Hemicelluloses (cellulosans) is the family name of polysaccharides that includes pentosans $(C_5H_8O_4)_n$, made up of the pentose units and hexosans $(C_6H_{10}O_5)_n$ made up of hexose units. The pentosans include such substances as xylan and araban which are hydrolysed to xylose and arabinose respectively. On dehydration, furfuraldehyde is formed:

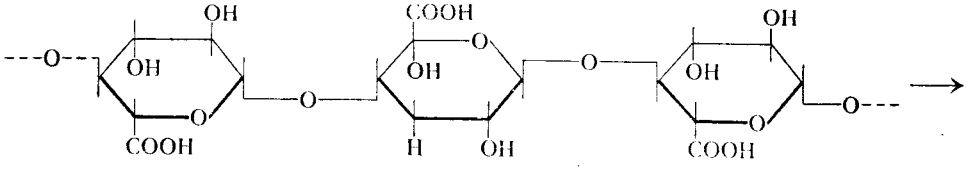


Pentose Furfural

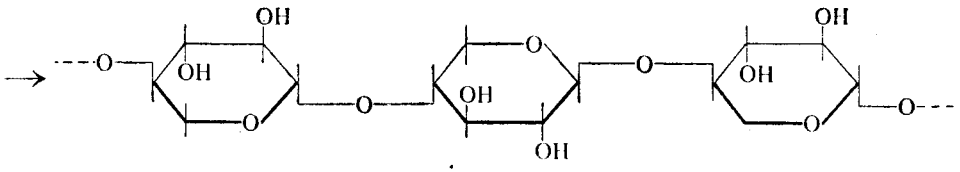
The notable hexosans are mannan and galactan.

The hemicelluloses also include the polyuronides, or polyuronic acids, for instance a polymer of a hexuronic acid such as galacturonic acid. There is a possible generic link between the polyuronides and the pentosans since the latter might be produced as the result of the decarboxylation of hexuronic acids. The possibility of transforming hexuronic acids into pentosans by the removal of carbon dioxide

molecules, and hence the conversion of hexosans into pentosans via these acids was first discussed by K. Smoleński [51]. It can be sketched as below:



Polyglucuronic acid



Xylan-(β-D-pyranoglucose)

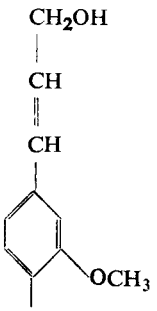
All hemicelluloses differ from cellulose in that they are soluble in dilute alkalis; it is self-evident that hexuronic acids dissolve particularly readily.

LIGNIN

Cellulose and lignin are the structural components of most plant cell walls. The constitution of lignin and its biosynthesis have been extensively studied but these problems are not yet solved.

Lignin is an ill-defined insoluble product of high molecular weight which is sensitive and therefore difficult to isolate in an unchanged form.

Already in 1897 Klason [52] suggested that gymnosperm lignin is derived from coniferyl alcohol. On the basis of experiments using isoeugenol as a model substance, Erdtman [53] advanced the hypothesis that lignin is a product of the oxidative polymerization of coniferyl alcohol:



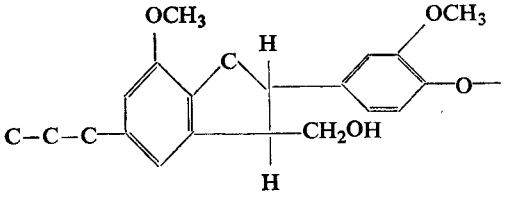
When the latter compound became easily available Freudenberg [54] studied its oxidation (mainly enzymatic) and obtained many crystalline compounds, believed

to be intermediates in the conversion of coniferyl alcohol into lignin, as well as amorphous lignin-like products believed to be closely related to lignin of wood. Similar work was done by Manskaya [55]. However, degradative studies by Hibbert [56], Freudenberg [57] and many others are in agreement with the assumption that lignin is built up from phenylpropane units joined either by oxygen atoms or by carbon–carbon links.

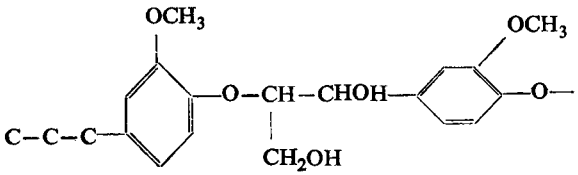
The presence of ether linkages were indicated by studies of Shorygin and Shorygina [58].

Present views on the structure of lignin are still largely speculative and in particular little is known of the non-aromatic parts of the molecules.

The occurrence in lignin of units such as:



A



B

is the subject of much discussion at the present time. Structure A shows how phenylpropane molecules could be joined by carbon–carbon links and B by ether linkages. The unit B contains a hydroxyl group in the α-position to the aromatic ring and such benzylalcoholic groups, according to Holmberg and Heden [60], account for many of the characteristic reactions of lignin, e.g. the formation of lignin sulphonic acids during the sulphite cooking process.

It is generally assumed that at least part of the lignin of wood is chemically bound to carbohydrates (hemicellulose).

Lignin gives characteristic colour reactions. With phloroglucinol and hydrochloric acid it turns red, with aniline sulphate, yellow.

CLASSIFICATION OF CELLULOSE

Cross and Bevan [59] suggested defining the pure cellulose content of a commercial cellulose in terms of its behaviour in the presence of a 17–18% aqueous sodium hydroxide solution. That part of commercial cellulose which is insoluble in this solution bears the name of α-cellulose and is the true cellulose. β- and γ-cellulose remain dissolved in the caustic soda solution. The difference between

these two fractions is shown by treating the alkaline solution with acetic acid, which causes β-cellulose to precipitate, whereas γ-cellulose remains in solution.

β-Cellulose is composed of cellulose with chains shortened by chemical treatment e.g. hydrocellulose, or oxidized cellulose (oxycellulose).

γ-Cellulose is mainly a hemicellulose fraction. The division into α-, β-, and γ-celluloses is a conventional classification.

Recently it received a certain physico-chemical justification as the result of Rånby's [46] work (p. 224). In any case it serves a useful purpose in practice. This method of classifying being widely used, as for example in order to estimate the value of a sample of chemical wood pulp for nitrating, when certain quantitative requirements concerning the minimum α-cellulose content are imposed.

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CHAPTER X

GENERAL CHARACTERISTICS OF NITROCELLULOSE

STRUCTURE OF NITROCELLULOSE

NITROCELLULOSE is obtained by esterification of cellulose with nitric acid. This process is described simply as nitration or more exactly O-nitration. The nitration of cellulose can be expressed by means of the following equation:

$$C_6H_{10}O_5 + xHNO_3 \rightleftarrows C_6H_{10-x}O_{5-x}(ONO_2)_x + xH_2O \qquad (4)$$

The cellulose formula in this equation is simplified by assuming the polymerization degree $n = 1$.

As with every reaction of esterification this process is a reversible chemical change. In addition to the fundamental process of esterification the opposite reaction of hydrolysis takes place, accompanied by a series of side reactions which result in the formation of various by-products. Thus a non-uniform, highly complex product is obtained.

The greatest number of (ONO_2) groups which can be introduced in relation to every six carbon atoms is three, as explained earlier in the chapter devoted to the structure of cellulose. The theoretical nitrogen content in such nitrocellulose, called "trinitrate", is 14.15%. This nitrogen content has been calculated for an empirical cellulose formula $C_6H_{10}O_5$. In point of fact, if the terminal rings with four hydroxyl groups are taken into consideration, the calculated theoretical maximum nitrogen percentage can be slightly higher, e.g. 14.17%. The longer the nitrocellulose chain, the lower this theoretical value.

In practice experiments to obtain a nitrocellulose with the theoretical nitrogen content failed, since a product of such high nitrogen content was readily decomposed, the nitrogen content falling to 13.5%.

The possibility of attaining a nitrogen content of 14.0% by nitrating with the help of nitric anhydride was indicated by Hoitsema [1]. His experiments have since been repeated and modified by many workers, as shown in the chapter on nitrating cellulose with nitric anhydride.

Nitrocellulose of 14.04% nitrogen was obtained by Berl and Rüff [2], when they nitrated cellulose with a mixture of nitric and phosphoric acid. Later Dalmon [3] has prepared nitrocellulose containing 14.12% of nitrogen by treating cellulose with gaseous N_2O_5.

Commercially produced nitrocellulose may have all the possible number of NO_2 groups, from 0 to 3 including the fractional ones. Moreover, the nitrogen content in a series of nitrocelluloses can vary continuously: a full series of cellulose nitrates can be obtained differing only by an insignificant variation in nitrogen percentage. In view of this fact, Eder [4] advanced the hypothesis that nitrocellulose was not one individual chemical compound but a mixture of several products. Eder postulated the existence of as many as six substances of different nitrogen content, namely: 14.15, 12.75, 11.15, 9.15, 6.75 and 3.75%.

This hypothesis could not explain, however, why such physical properties as solubility and viscosity in the instance of, say, nitrocellulose containing 13.45% of nitrogen, which Eder assumed to be composed of equal parts of nitrocelluloses 14.15 and 12.75%, are not the average properties of the components. Besides Eder could not explain why high nitrated cellulose, with 14.15% N, in general a chemically unstable substance, decomposed to form a 13.5% N nitrocellulose. In accordance with Eder's views the decomposition should have gone on until the content of nitrogen was 12.75% i.e. to the nearest nitration degree.

In order to express the chemical formula of nitrocellulose, for some time formulae suggested by Vieille [5], were generally used in which a polymerization degree of nitrocellulose $n = 4$ was proposed:

$$C_{24}H_{40-x}C_{20-x}(ONO_2)_x$$

x having any value up to 12.

A more exact formula including a variable polymerization degree p, would be as follows:

$$[C_{24}H_{40-x}O_{20-x}(ONO_2)_x]_p$$

By treating cellulose with nitric acid or nitrating mixtures of different composition Vieille [5] isolated a range of nitrocellulose samples containing a number of (ONO_2) groups lying very close to the values $x = 4$ and $x = 12$. He named the different nitrocelluloses according to the parameter x by applying a suitable prefix (Table 37).

TABLE 37

x	Name	Formula	Nitrogen content, %
12	Cellulose dodecanitrate	$C_{24}H_{28}O_8(ONO_2)_{12}$	14.15
11	Cellulose endecanitrate	$C_{24}H_{29}O_9(ONO_2)_{11}$	13.45
10	Cellulose decanitrate	$C_{24}H_{30}O_{10}(ONO_2)_{10}$	12.75
9	Cellulose enneanitrate	$C_{24}H_{31}O_{11}(ONO_2)_9$	11.96
8	Cellulose octanitrate	$C_{24}H_{32}O_{12}(ONO_2)_8$	11.11
7	Cellulose heptanitrate	$C_{24}H_{33}O_{13}(ONO_2)_7$	10.16
6	Cellulose hexanitrate	$C_{24}H_{34}O_{14}(ONO_2)_6$	9.15
5	Cellulose pentanitrate	$C_{24}H_{35}O_{15}(ONO_2)_5$	8.00
4	Cellulose tetranitrate	$C_{24}H_{36}O_{16}(ONO_2)_4$	6.76

Today Vieille's formulae are regarded as purely conventional though useful in arranging various types of nitrocellulose into classes. Nevertheless, many authors have tried to isolate definite substances corresponding to Vieille's compounds. Thus de Bruin [6] claimed that he had isolated definite compounds containing 11.97 and 12.76% of nitrogen, corresponding to the enneanitrocellulose and decanitrocellulose of Vieille.

At present a less complicated nomenclature, based on the average number of (ONO_2)-groups attached to one anhydroglucose ring, is accepted:

cellulose trinitrate	$C_6H_7O_2(ONO_2)_3$	14.15% N
cellulose dinitrate	$C_6H_8O_3(ONO_2)_2$	11.11% N
cellulose mononitrate	$C_6H_9O_4(ONO_2)$	6.76% N

Nitrocellulose of 12.65% N, according to this nomenclature, is called 2½-nitrate, etc. The degree of nitration can also be designated by the "degree of substitution" (D.S.) which is the average number of nitrated hydroxyl groups in one anhydroglucose unit.

This manner of determining the share of esterified groups results partly from the X-ray studies on nitrocellulose, because it has been proved that only the high nitrated cellulose, i.e. trinitrate, gives a wholly sharp definite picture. Other cellulose nitrates manifest a composite X-ray picture looking as if it were formed by superposing an X-ray picture of cellulose on that of its trinitrate. This observation led to the view that every cellulose with a lesser nitrogen content than cellulose trinitrate represented a mixture of trinitrate with non-nitrated cellulose. This idea was suggested by the first X-ray investigators of cellulose: Herzog and Náray-Szabó [7], Náray-Szabó and Susich [8], and particularly by Hess and Trogus [9]. The fact that neither non-nitrated cellulose nor cellulose trinitrate have ever been separated from nitrocellulose, nor even a low-nitrated cellulose is a weighty argument against this suggestion.

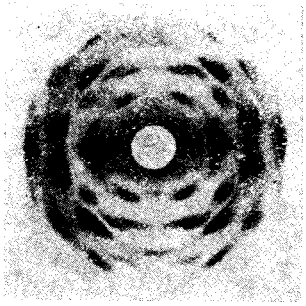
The earlier view has therefore been modified to suggest that every nitrocellulose is composed of anhydroglucose rings with three nitrate groups attached, containing 14.15% of nitrogen, and of non-nitrated and partly nitrated anhydroglucose rings. This view is generally accepted and the diagrammatic presentation shown in Figs. 86 and 89 is discussed below.

Among other X-ray investigations, the publications of Trillat [10], of Berl and Hefter [11] and of Champetier [12] should be mentioned.

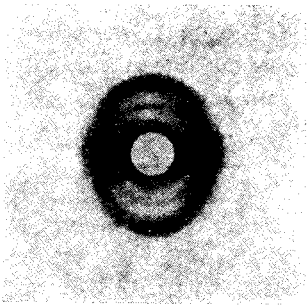
The studies of Miles and Craik [13] merit special attention since they obtained the following X-ray diagrams of ramie (Chinese nettle) cellulose, which is notable for a distinctly crystalline structure (Fig. 83).

The dimensions of a nitrocellulose crystal cell depend on the degree of nitration. Values from the papers of Mathieu [14, 34] characterizing native cellulose and various nitrocelluloses are quoted in Table 38.

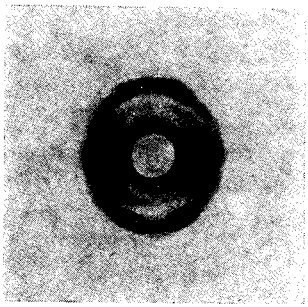
According to Mathieu, trinitrocellulose crystals belong to the orthorhombic system, the dimensions of the crystal cell being: $a = 12.40$ Å, $b = 25.4$ Å, $c = 9.0$ Å, angle $\beta = 90°$. Similar figures have been reported by Happey [15].



(a)



(b)



(c)

FIG. 83. X-Ray diagrams (according to Miles and Craik [13]): (a) ramie cellulose, (b) ramie cellulose dinitrate, (c) ramie cellulose trinitrate.

TABLE 38

Native cellulose $a = 8.35$ Å $cb = 7.40$ Å	$A_4(002)$ $d = 3.93$ Å	$A_1(101)$ $d = 5.46$ Å $A_2(101)$ $d = 6.06$ Å
Nitrocellulose		
10.54% N	$A_2^d = 4.00$ Å	$A_1^d = 6.84$ Å
11.46		6.93
12.30		7.08
12.66		7.13
12.90		7.15

According to Trommel [15a] nitrocellulose exists in two structural forms:

(1) Intermediate structure characterized by cell dimensions $a = 13.81$ Å, $b = 10.45$ Å, $c = 7.92$ Å, $\beta = 90°$. The structure closely resembles that of cellulose and some cellulosic structural elements are present. The nitrate groups are located between the glucose rings in line with the a-axis. This structure exists between 12.3 and 13.2% N.

(2) Trinitrate structure with cell dimensions $a = 12.94$ Å, $b = 25.66$ Å, $c = 8.92$ Å. The chain molecules are paralled to the b-axis. It is formed with great difficulty but once formed it remains stable, even after denitration.

A plane projection of the crystal cell of cellulose (a) and of cellulose trinitrate (b) is outlined by the schemes in Fig. 84. Much interest was aroused in the results

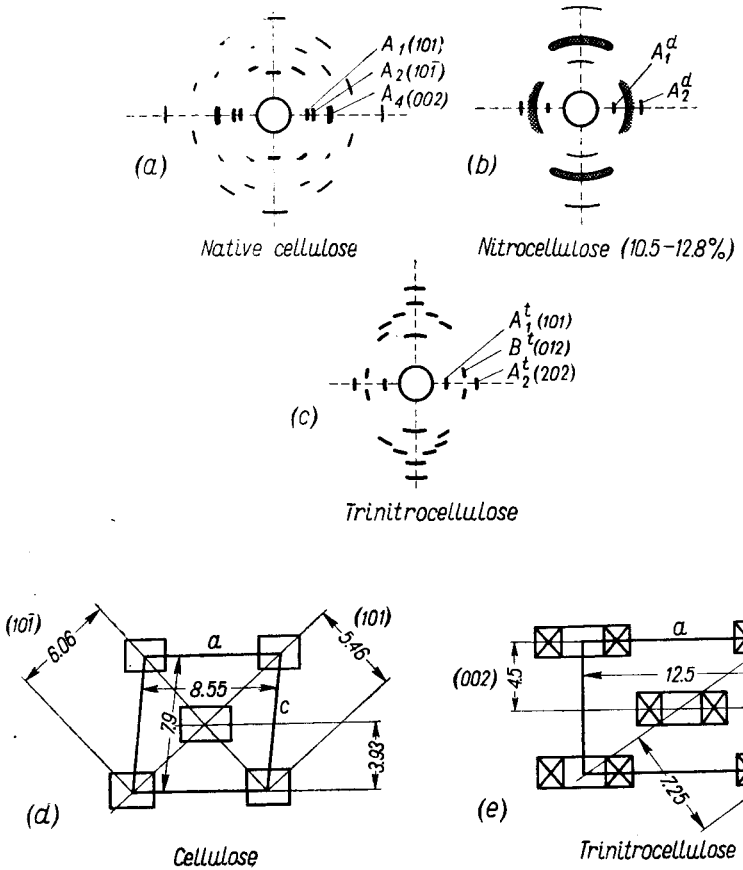


FIG. 84. X-Ray fibre diagrams (a, b and c), cell projections of cellulose (d) and cellulose trinitrate (e) by Mathieu [34].

obtained by Miles [16] who examined the crystal cell dimensions along the equatorial axis (101) for nitrocellulose obtained by nitration and denitration (Table 39).

The spatial configuration, extended in consequence of nitration, is retained despite partial denitration. This is why the cell size of a denitrated cellulose is larger than that of nitrocellulose containing the same nitrogen percentage, but obtained by a direct nitration of cellulose.

These results were confirmed by Trommel [15a] who expressed the change of the 101-spacing with increase of the nitrogen content graphically (Figs. 85 and 86).

TABLE 39

THE DIMENSIONS OF THE NITROCELLULOSE CELL UNIT ALONG THE (101) AXIS

Examined product	Nitrogen, %	*d*,Å
Cellulose nitrated to	11.14	6.67
Cellulose nitrated to	12.77	6.85
Cellulose nitrated to	13.57	7.25
Nitrocellulose 13.75% N, denitrated to	11.52	7.10
Nitrocellulose 13.75% N denitrated to	10.42	7.05

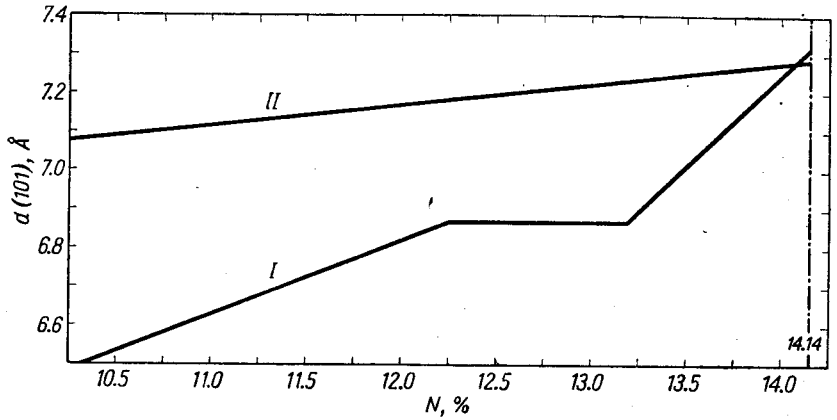


FIG. 85. 101-spacing of nitrated cellulose (*I*) and partly denitrated trinitrocellulose (*II*) according to Trommel [15a].

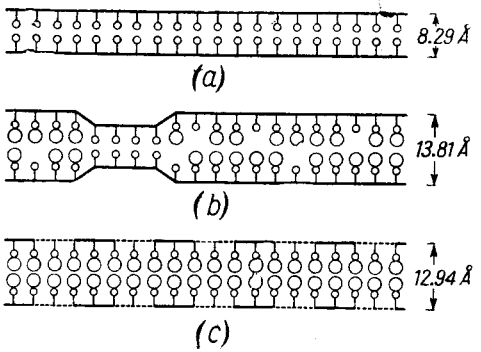


FIG. 86. Diagrammatic presentation of cellulose (a), intermediate structure (b) and trinitrate (c) chains, according to Trommel [15a].

His diagram shows the existence of the intermediate structure between 12.3 and 13.2% N and the two-phase system between 13.2 and 14.1% N, and also indicates (Fig. 85) that once the trinitrate structure has been formed, it persists even when a considerable number of nitrate groups have been removed. Because of the increase of the distance along *a*-axis, the hydrogen bonds —O—H···O— which exist in cellu-

H

lose and cellulose dinitrate are not present in denitrated cellulose trinitrate, according to Trommel [15b], or are weakened. At the same time the X-ray diagrams of nitrocelluloses having a complete range of nitrogen content were studied by Miles and Craik [13]. According to these authors the products of nitration of cellulose can be divided into three classes:

(1) Those containing less than 7.5% N, which show a fibre character and give no X-ray diffraction indicating nitration, but only those of mercerized cellulose.

(2) Those containing between 7.5 and 10.5% N. They are more or less disintegrated, yielding very diffuse diffractions, apparently due in part to very small crystalline elements of mercerized cellulose.

(3) Those of more than 10.5% N giving diagrams which indicate the crystalline character of the structure, increasing as the nitrogen content increases until eventually a critical point at 12.8% is reached when the sharply defined diagram characteristic of cellulose trinitrate makes its appearance. On the basis of these experiments Miles and Craik presented the following picture of cellulose nitration. In the first stage of nitration (stage I) the nitric acid penetrates the whole of the cellulose structure (otherwise it could not be mercerized), nitration occurring only in the disordered amorphous regions. As the acid concentration is increased, the nitration gradually invades the ordered regions (stage II). At the same time the micellar arrangement is almost entirely broken down.

Swelling and breakdown of the micellar arrangement takes place in final stage of nitration (stage III), but to a diminished extent as the acid concentration increases. The number of the nitrate groups increases with the acid concentration but in a random manner, so that crystalline arrangement is at first difficult. It is facilitated as the nitrate groups accumulate and when 12.8% N is reached there are so many ONO_2 groups that an orderly arrangement of chains becomes possible and there is a sudden registration of the trinitrate structure.

Meyer and Mark [17] reached a similar conclusion on the basis of their own experiments and the results of other authors.

Mathieu [18] has shown that X-ray diagrams taken at frequent intervals during nitration of cellulose with N_2O_5 vapour indicate that the structure progresses through all the stages from cellulose to cellulose trinitrate.

Taking into account both their own X-ray investigations and those of other workers, Meyer and Mark [17] came to the conclusion that indistinct pictures of cellulose nitrates having a lower nitrogen content than cellulose trinitrate and hence containing free hydroxyl groups, occur due to the statistically irregular distribution

of esterified hydroxyl groups. This explains why composite pictures that appear to be created by superposition of the cellulose picture upon that of trinitrate, are found in the X-ray diagrams.

The X-ray experiments of Hess and Trogus [19] have shown that nitrocellulose immediately after formation gives a very diffuse X-ray diagram with barely legible interference bands, typical for swollen cellulose and nitrocellulose.

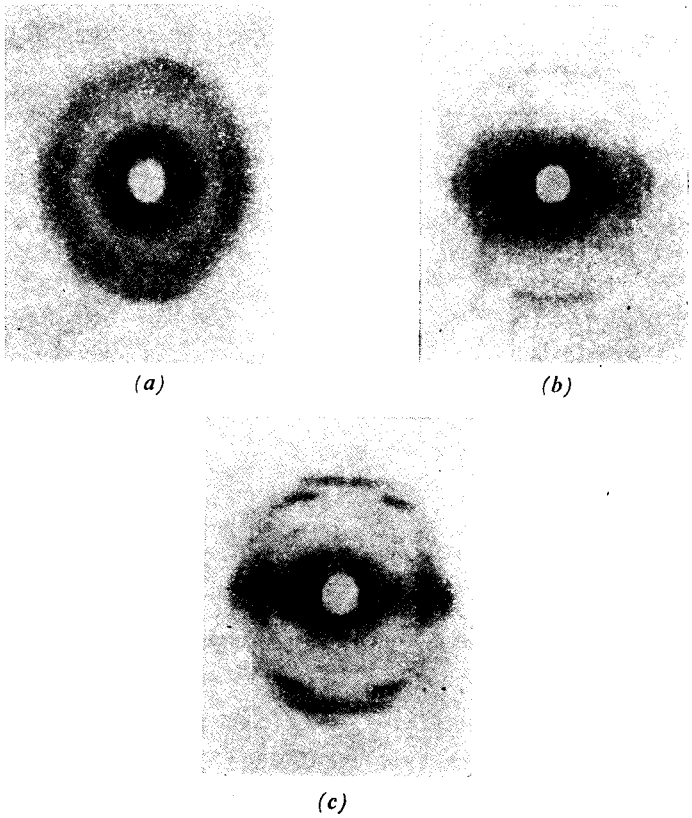


FIG. 87. X-Ray diagrams: (a) of nitrocellulose immediately after the separation from the nitrating acid, (b) of nitrocellulose after washing out the acid, (c) of stabilized nitrocellulose (Hess and Trogus [19]).

The interference bands grow more and more distinct, however, as nitrocellulose is washed, until after stabilization boiling, a picture with very sharp rings is obtained, as shown in Figs. 87 a, b and c.

Herzog and Londberg [20] have examined the X-ray diagrams of cellulose produced by denitration of a carefully nitrated product. The picture of the regenerated cellulose was in principle identical with that of cellulose before nitration. This observation suggests that a cautious nitration of cellulose that proceeds without oxidation or hydrolysis does not change the microcrystalline structure of the cellulose, i.e. this is a topochemical reaction, in which the product preserves the same

crystalline structure as the original substance. Among inorganic substances, a similar reaction is that between NaOH and cupric nitrate. The cupric hydroxide formed shows the same crystallographic properties as the original compound differing only in crystal size since one large crystal is make up of a considerable number of the small ones. Similarly ion-exchange processes depend on the ability of permutits, which are artificially produced silicates, natural crystal zeolites and ion-exchange resins, to absorb from solutions certain cations and to return to the solutions other cations contained in the silicate and the resins respectively.

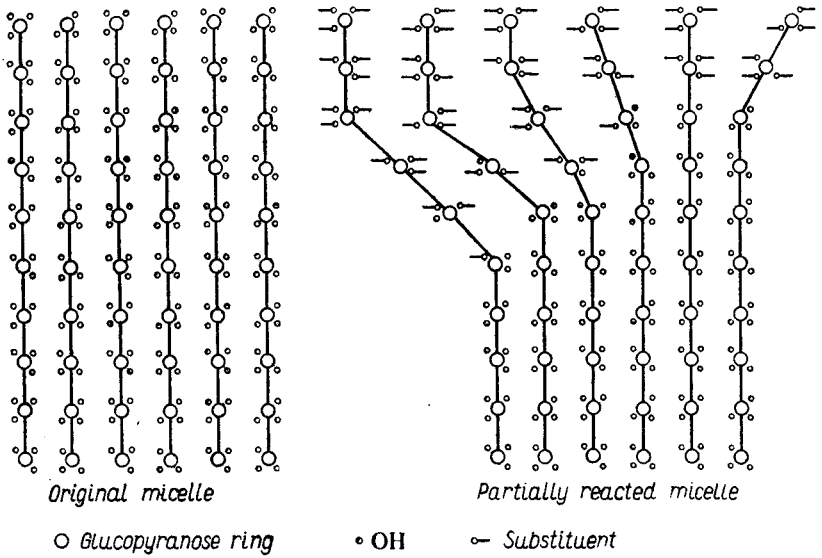


FIG. 88. Diagram of esterification of cellulose (Spurlin [21]).

The amorphous part of cellulose is regarded as more reactive than the crystalline part. When the crystalline part enters into a reaction, as for instance, in swelling or nitrating, its structure can undergo certain changes, as swelling causes the micelle chains to expand. An outline of the process suggested by Spurlin [21] showing how the micelles react with an esterifying agent is shown in Fig. 88 which indicates how the reagent attacks one end of the micelle and a gradual sliding apart the chain ensues.

PHYSICAL PROPERTIES OF NITROCELLULOSE

MELTING POINTS

Newman [22] has estimated indirectly the melting point of nitrocellulose containing 12.6% N by the following method. He determined the melting points of mixtures of nitrocellulose and γ-butyrolactone obtaining values from 39 to112°C. By extrapolation he calculated the melting point of nitrocellulose to be 890°K, i.e. 617°C.

The calculated heat of fusion is 1350 cal per anhydroglucose unit, and the corresponding entropy of fusion is 1.51 cal/°C.

SPECIFIC GRAVITY

Earlier authors: Wehrhahn [23] and Mosenthal [24], assumed that the specific gravity of nitrocellulose determined in water is independent on the nitrogen content, and is 1.66. For cellulose in alcohol, Mosenthal reports the value 1.56–1.58. The specific gravity of nitrocelluloses of different nitration degree has been determined by Brunswig [25].

For a nitrogen content of 11.10% he found the specific gravity to be 1.653, whereas for a nitrogen content of 12.30 and 13.20% N the value was 1.654 and 1.659 respectively.

Values measured later in the Chemisch-Technische Reichsanstalt [26] are well in line with those reported earlier. The increase of specific gravity accompanying the increase of nitrogen content is extremely small, namely:

nitrogen content, %	specific gravity at 15°C	
	in xylene	in water
11.61	1.616	1.655
11.73	1.622	1.655
12.20	1.630	1.655

For the specific gravity determined in a pycnometer with mercury, a series of diminishing figures has been established:

nitrogen content, %	specific gravity
11.61	1.680
11.73	1.666
12.20	1.660

The determination of the specific gravity of nitrocellulose is beset with difficulty, since the result depends to a considerable extent upon the capacity of the liquid used for measurement to penetrate into the interior of the colloidal structure of the fibre. Petitpas and Mathieu [27] have estimated the specific gravity of trinitrocellulose at 20°C in various liquids:

paraffin oil	1.608
benzene	1.636
cyclohexane	1.644
water	1.669
ethanol	1.696

For the specific gravity of nitrated products in water following data were reported by the same authors:

nitrogen content, %	specific gravity
11.52	1.654
11.9	1.659
12.2	1.674
13.1	1.662

SOLUBILITY

Esters and ethers of cellulose, and especially nitrocellulose, are most widely used in the form of a colloidal solution. This technique is applied in the manufacture of smokeless powder, nitrocellulose varnishes, film and celluloid.

Nitrocellulose will dissolve in many solvents, e.g. acetone, acetic esters, ether–alcohol. There also exist types of nitrocellulose soluble in ethyl alcohol alone.

Non-volatile solvents are usually called "gelatinizers" (or "plasticizers" in plastics technology).

The solubility of nitrocellulose in a solvent is defined by the percentage in this nitrocellulose of the fraction soluble in the solvent in question.

Thus the expression "solubility" of nitrocellulose in a certain solvent has a different meaning from the concept of solubility as applied to a crystalline substance able to form a saturated solution.

Solutions of cellulose, its esters and ethers are colloidal solutions. They are reversible lyophilic colloids. The most important characteristics of such solutions are as follows.

(1) The dissolved substance is precipitated with difficulty from the dispersing phase. Having been precipitated, it can be redissolved. The precipitated phase contains much dispersing phase.

(2) Prior to dissolution the substance undergoes swelling.

(3) The viscosity of the solutions is high, even if the concentration is low.

(4) The substance does not form saturated solutions in a single solvent, hence it has no limits of solubility in the usual sense of this term as applied to crystalline bodies. A solution resembling in its properties a saturated one can be prepared by means of a binary solvent, where a liquid immiscible with nitrocellulose is one of the two components (e.g. acetone and water).

Formerly it was believed that in their physical properties, as for instance no increase in boiling point and in osmotic pressure, colloidal solutions of cellulose derivatives were radically different from solutions of crystalline substances having small molecules. Now, however it is clear that the difference is not so considerable and that a close analogy exists between solutions of cellulose and its derivatives and those of substances of low molecular weight.

Thus analogy is visible even in the first stage of dissolution, i.e. in swelling. If acetone is added to a suspension of nitrocellulose in benzene, nitrocellulose starts to swell, increasing in volume, finally dissolving when a sufficient amount of acetone is added. The swollen nitrocellulose phase can be regarded as a solution of solvent in a solid phase. The water layer of a water–benzene system behaves the same way when alcohol is introduced to the system. Namely, as long as alcohol is added the water layer increases in volume, i.e. it "swells" whilst the benzene layer remains almost unchanged. After a certain amount of alcohol has been added the benzene layer joins with the other phase to form a homogeneous solution. Nitrocellulose can be compared with the water layer in this example.

The process of dissolving nitrocellulose fibres in non-volatile solvents, that are commonly used in small quantities to bring about the transition of nitrocellulose fibres in a solubilized state, is often called gelatinization.

Microscopic investigations of the gelatinization and dissolution of nitrocellulose seem to indicate that a protective cover exists on the surface of nitrocellulose fibres which dissolves with difficulty (Mangenot and Raison [134], Fenson and Fordham [133], p. 286).

According to investigations reported by Jenkins and G. Davies [28] and by T. Urbański [29] the dissolution and gelatinization of nitrocellulose begins at the ends of fibres cut in the beating process.

The viscosity of nitrocellulose solutions provides a further example of analogy. It has been demonstrated by examining the viscosity of solutions prepared from low-molecular substances that the higher the molecular weight, the greater the viscosity. Staudinger [30] established his rule for substances with small molecules. Subsequently it was proved that his law can also be applied to long-chain high molecular weight substances such as cellulose derivatives.

Detailed experiments on the osmotic pressure of cellulose solutions (Kratky and Musil [31]) have shown that the osmotic pressure of cellulose derivatives is subject to rules which do not differ from the laws for ideal solutions. The equation of osmotic pressure

$$\frac{P}{c} = \frac{RT}{M}(1 + Bc - Cc^2 + \ldots)$$

where P represents the osmotic pressure, c — concentration, M — molecular weight, and B and C are constants independent of the polymerization degree, is valid for solutions of substances of high-molecular weight as well as for those of low-molecular weight provided that the mass concentrations are uniform.

The divergencies observed with high-molecular weight substances are caused by the fact that when the value of M is large the pressure P becomes insignificant, hence the experimental error is large.

Assuming that in principle manifold similarities exist between the solutions of low-molecular weight substances and the solutions of cellulose derivatives, the hypothesis has been formulated that in a cellulose derivative solution the molecules are associated into large aggregates — micelles. In this way micelles which are assumed to be present in cellulose and its derivatives in the solid state were thought to exist also in solution, individual molecules in the solution being bound together by van der Waals or electrostatic forces. This idea has been used to explain numerous properties of colloidal solutions of inorganic substances and of soaps. Nevertheless it was realized that inorganic salts and soaps carry strong electric charges whereas nitrocellulose solutions are almost completely electrically neutral.

These views have now been abandoned in favour of the hypothesis advanced by Staudinger [30] that only individual molecules are present in a solution forming no larger aggregates. In point of fact particular molecules are capable of combining

among themselves by means of residual bonds (van der Waals forces), but these linkages are unstable and are readily broken as the result of the thermal motion of the molecules.

One of the arguments against the existence of micelles in solutions of cellulose derivatives is the fact that when cellulose is converted into its derivative, e.g. an ester, the degree of polymerization remains almost unchanged. This however only occurs when ester formation is carried out under strictly controlled conditions (nitration at low temperature with nitric and phosphoric acids mixture — p. 341, or with nitric, acetic acids and acetic anhydride mixtures — p. 344). The relevent data found by Staudinger and Mohr [32] are collected in Table 40.

TABLE 40

THE DEGREE OF POLYMERIZATION OF CELLULOSE AND NITROCELLULOSE

Polymerization degree of cellulose (determined by measuring the viscosity of cuprammonium solution)	76	186	254	450	720	1540	2550
Polymerization degree of nitrocellulose (determined by measuring the viscosity of acetone)	77	170	220	440	670	1360	2500

If micelles were present in both types of solutions, we would have to assume different forces binding different cellulose derivatives, hence viscosity measurements should give different molecular weights. However the results disagree with those obtained by Gralen and Svedberg [32a], and reported on p. 343.

Solutions of cellulose derivatives, such as nitrocellulose, passed through a fine porous filter demonstrate neither the Tyndall effect, nor the presence of particles visible in the ultra-microscope. This is one more piece of evidence that the properties of these solutions are the same as those of substances with low molecular weight. The same holds for cellulose in ammoniacal solutions of cupric oxide ("cuprammonium").

The nature of solubility and the "strength" of solvent. According to present views the dissolution of cellulose esters consists in the separation of the chain-molecules under the specific influence of the solvent until all bonds between the chains disappear. The macromolecules of polymer can slide apart even at the swelling stage. Because of their elasticity, it is possible that the chains can be pushed aside in certain places or along the entire molecules. Further, a shortening of chains occurs, but being a secondary effect it proceeds slowly.

In certain cases dissolution does not take place, the action of the solvent being limited to the production of swelling, due to insufficient "strength" of the solvent. This is possible in two events.

(1) If nitric groups are substituted for the hydrogen atoms of cellulosic hydroxyl groups only to an inappreciable extent then the constitution of the chains is regular enough to ensure a great probability that two hydrogen atoms in neighbouring macro-molecules will be close enough to link the two chains together. Hence a low nitrated cellulose may swell in contact with ether–alcohol but will not dissolve.

(2) If all or nearly all the hydroxyl groups are esterified (as in cellulose trinitrate), then the long-chain-molecules again possess a regular structure, and under the influence of forces of adhesion (van der Waals bonds) close mutual contact may be maintained (Fig. 89a). Here again the solvent may be "too weak" as to push aside

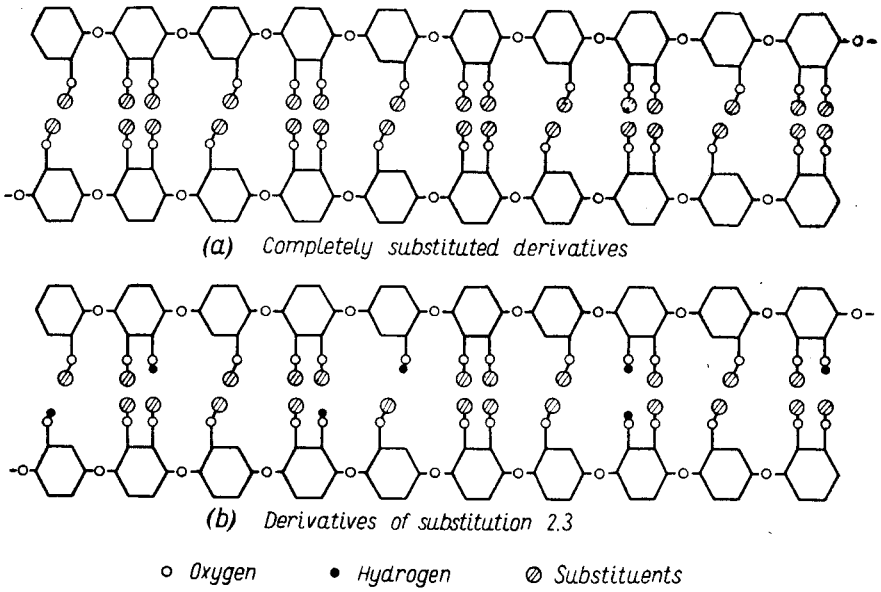


FIG. 89. Influence of complete (a) and partial (b) esterification on contact between cellulose chains according to Spurlin (in Ott and Spurlin [33]). Only substituents between chains are shown; oxygen atoms not shown in rings.

such chains, and in fact high-nitrated nitrocellulose is not soluble in a mixture of alcohol and ether (Spurlin [33]).

On the other hand, in the case of cellulose dinitrate or 2½-nitrate, the structure is generally irregular, hence no adhesion between the chains exists. With a small number of irregularly distributed hydroxyl groups there exists little probability that the macro-molecules could be joined together by means of hydrogen bonds (Fig. 89b, see also Figs. 86 and 88).

According to Trommel [15b] the cellulose dinitrate chains become more irregular after being dissolved in acetone and precipitated with water. Hence the solubility of precipitated cellulose dinitrate is increased [15c]. The proposed relationship between the solubility and regularity of the structure of nitrocellulose has been confirmed by experiments with nitrocellulose at different stages of swelling and

dissolution. Thus, it has been established by Mathieu [34] and Petitpas [35] on the basis of X-ray analysis that adding small amounts of solvent, e.g. acetone, cyclopentanone, methyl nitrate, to nitrocellulose, causes an increase in the distance between the nitrocellulose chains. The distance grows larger until one molecule of solvent is absorbed in proportion to every anhydroglucose unit after which further addition of solvent does not bring about any further increase in the distance between the macro-molecules. Finally the fibrous structure disappears completely when one molecule of solvent to one (ONO_2) group-equivalent has been added.

On the other hand, numerous observations favour the opinion that the solvent enters into a chemical combination with nitrocellulose to form solvates. Some of those solvates are stable only at low temperatures. For instance, cellulose dinitrate does not dissolve in methyl alcohol at room temperature, though on cooling it does so. The cellulose nitric ester precipitates again when the solution is heated. Similar behaviour is observed with ethyl alcohol: a lower temperature causes nitrocellulose to swell or even to dissolve more readily. The solvent seems likely to be bound to free hydroxyl radicals (Highfield [36]). The hypothesis explains why nitrocellulose is soluble in a mixture of ether and alcohol, though neither of these solvents, when used separately, is capable of dissolving it. It is assumed that first an alcohol solvate of nitrocellulose is formed which then dissolves in the ether.

The hypothesis that nitrocellulose is capable of forming solvates with certain solvents has been confirmed by X-rays analysis. Hess *et al.* [37] have established that nitrocellulose reacts to form microcrystalline addition compounds with many solvents: acetone, methyl nitrate, cyclohexanone, cyclopentanone and camphor. Despite the fact that other workers (Desmaroux and Mathieu [38]) have not fully confirmed the results of Hess's experiments, they are most probably correct.

As evidence that nitrocellulose forms compounds with solvents the fact is quoted that when nitrocellulose is dissolved heat is evolved. It has been established by Okatov and Emmanuilova [39] that in the boundary layer of the solid nitrocellulose phase and the liquid ether–alcohol phase heat is developed by the following processes which occur in turn: wetting of the nitrocellulose fibres, formation of the solvate, swelling and dissolution. Those solvents which evolve the greatest heat of wetting and solvatation, are also characterized by a greater ability to bring about the swelling and dissolution of nitrocellulose. Thus, with an ether–alcohol mixture of 1:1 ratio, a considerably larger amount of solvatation heat is developed than with ether alone. The values of the heat produced by dissolving a film made from nitrocellulose of 11.9% of nitrogen content, and treated with different solvents, determined by Lipatov and Meyerson [40] are collected in Table 41. (For more details about the absorption heat of the solvent see p. 284). Investigations into the absorption isotherms of solvent in nitrocellulose are of considerable importance in relation to the problem of which essential factors cause nitrocellulose to bind solvents.

Two methods of investigating the ability of nitrocellulose to sorb substances which dissolve it are in use. One consists in placing nitrocellulose in an atmosphere

TABLE 41

HEAT OF SOLUTION OF NITROCELLULOSE

Type of film and solvent	Heat of solution (cal per gramme of the solvent) for solution of concentration:	
	15%	2%
Film including 2.4% water	—	—
CH_3COCH_3	19	13
$CH_3COOC_2H_5$	16	13
Dry film — CH_3COCH_3	20	19

containing vapours of the solvent being examined at a vapour pressure lower than the saturation pressure at the temperature for which the sorption isotherm is to be determined. The other method consists in drowning nitrocellulose in a solution composed of the solvent and another non-solubilizing liquid (diluent). The amount of solvent absorbed by nitrocellulose is then estimated.

It is evident that only the second of the two methods can be applied if a non-volatile solvent (gelatinizer) is being tested.

The amount of the substance absorbed (x) can be defined either as a percentage or as a proportion of the sorbent (m) thus by a ratio of $x/m \cdot 100\%$ or by x/m. Furthermore it may be expressed as the molecular ratio n_1/n_2 of the absorbed substance to the sorbent, or as the proportion of absorbed molecules to the total number of molecules: $N = n_1/(n_1+n_2)$.

The absorption isotherms of acetone in nitrocellulose containing 11.6 and 13.5% N respectively at 40°C have been studied by Desmaroux [41]. Acetone was dissolved in castor oil. In a separate series of experiments, Desmaroux has established the vapour pressure of acetone dissolved in castor oil, hence the activity of acetone vapour, defined as the ratio of acetone vapour pressure of the respective solution to the vapour pressure of pure acetone. Curves illustrating the relationship between the number of acetone equivalents absorbed by one anhydroglucose unit (C_6) equivalent of nitrocellulose, and the activity of the acetone vapours are shown in Fig. 90.

Miles [42] has followed the absorption of acetone from aqueous solutions, obtaining the results shown in Fig. 91.

The question whether the absorption of acetone vapours at 30°C was dependent on the nitrogen content of nitrocellulose was investigated by Rubenstein [43] (and Jenkins, Bennett and Rubenstein [122]). Figure 92 outlines the results: the acetone to nitrocellulose weight ratio as well as the mole proportion of acetone to anhydroglucose unit ("submole of nitrocellulose").

The experiments on the absorption of different alcohols, ether, and butyl acetate, carried out by McBain *et al.* [44] and those on absorption of ether–alcohol mixtures by Desmaroux [45] are also noteworthy.

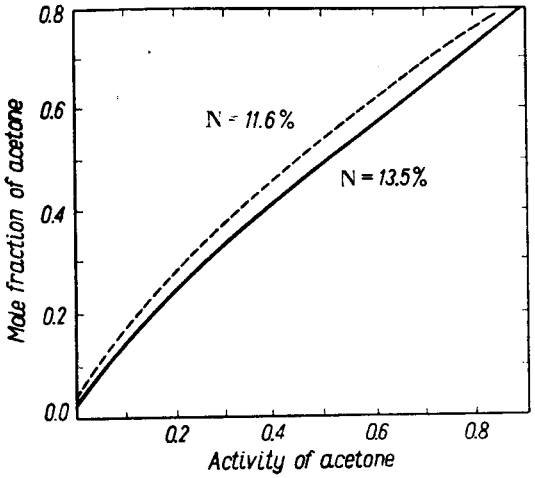
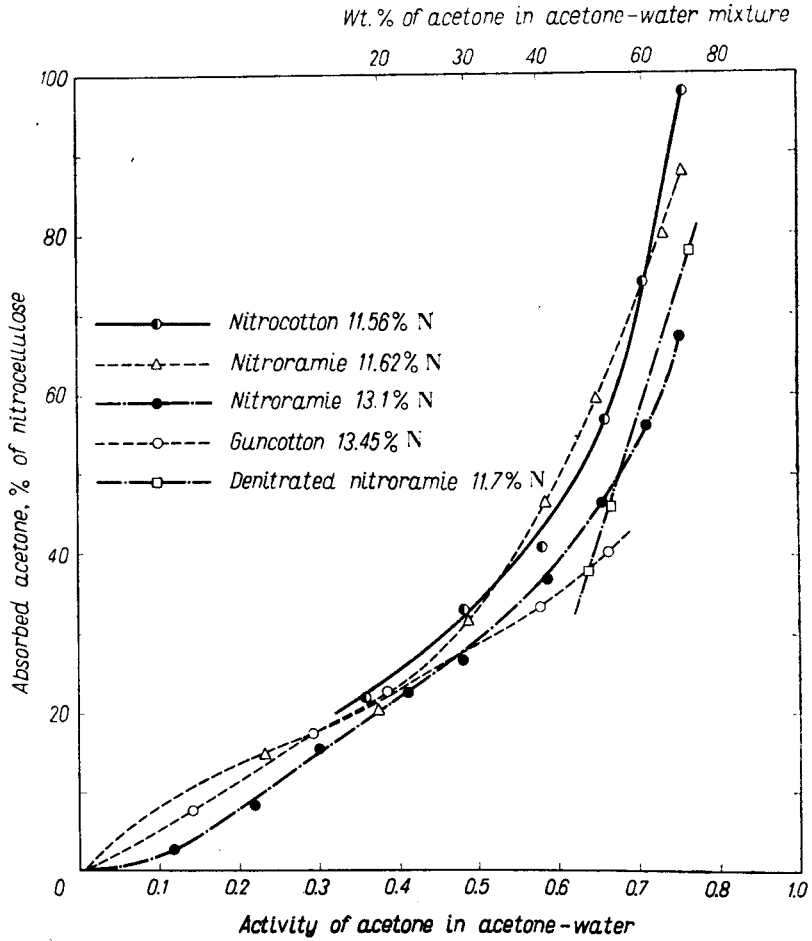


FIG. 90. Relationship between the number of moles of acetone absorbed by nitrocellulose and the activity of acetone vapour, according to Desmaroux [41].



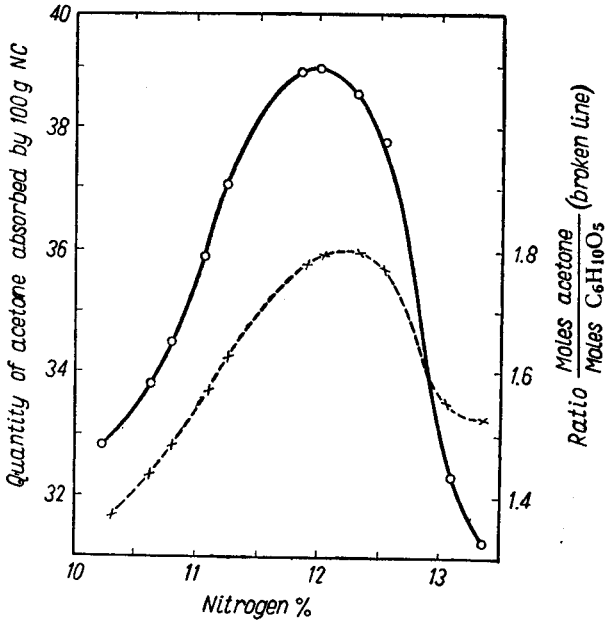


FIG. 92. Absorption of acetone by nitrocottons of various nitrogen content, at the acetone activity of 0.64 according to Rubenstein [43].

Absorption isotherms of such important gelatinizers as carbamite (centralites) and camphor in petroleum ether (Fig. 93) were published by Desmaroux [46].

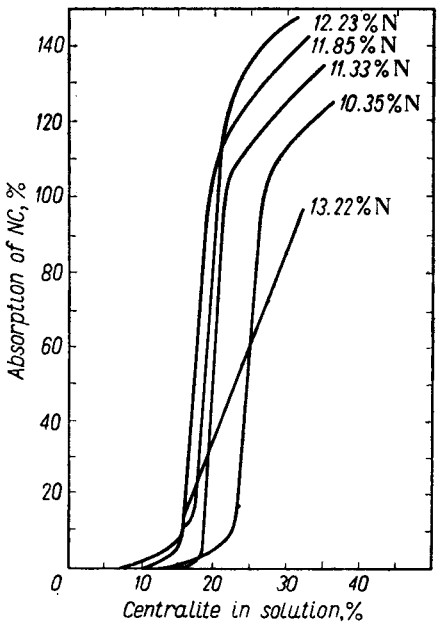


FIG. 93. Absorption isotherms of carbamite (ethyl centralite) (from hexane) by nitrocelluloses, according to Desmaroux [46].

G. G. Jones [47] has obtained similar graphs for camphor, tricresyl phosphate and dibutyl phthalate.

Desmaroux has also determined the nitroglycerine absorption isotherms from its chloroform and acetone solutions at 20°C by a nitrocellulose with a nitrogen content of 11.2–13.35 and 14.2% N (Figs. 94a and 94b respectively) as well as those of nitroglycol in an ethyl ether solution at 20°C sorbed by nitrocellulose of 12.2% N as shown in Figs. 95a and 95b.

More recently the absorption of methyl and ethyl nitrates from the gaseous phase at 40°C by nitrocellulose of 12% N, was examined, the results being shown in Fig. 96 (Petitpas and Mathieu [27]).

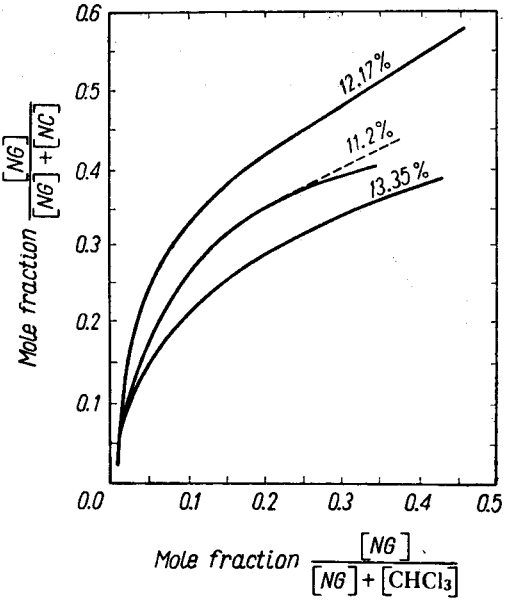
In order to see whether the solvent, or gelatinizer, formed addition compounds with nitrocellulose, several investigators have examined the X-ray diagrams of nitrocellulose previously treated with solvents. The first experiments in this field were those of Hess, Trogus and Tomonari [37]. They examined nitrocellulose that had absorbed acetone from its solution in ligroin ("compound I") or from its water solution ("compound II") and concluded that in both cases addition compounds were formed. This was confirmed by the fact that the X-ray diagrams of nitrocellulose treated with acetone differed from those of nitrocellulose itself. Furthermore, the diagram of "compound I" differed from that of "compound II", both with regard to the number of spots and their sharpness. According to Hess *et al.* the addition product contained three molecules of acetone to each molecule of anhydroglucose. The authors have also studied the X-ray diagrams of nitrocelluloses treated with other ketones, e.g. cyclohexanone, camphor, etc.

Later, X-ray diagrams given by nitrocelluloses with acetone prepared after the Desmaroux method by absorbing acetone from castor oil solutions, were examined by Mathieu [34]. The spacing of the plane A_1^d (101) (Fig. 84, Table 38) was 7.25 Å for trinitrocellulose, and less than 7 Å for nitrocellulose of 11.6% N. However, the distance in both types of nitrocellulose is increased considerably as acetone is absorbed, approaching 11 Å when the acetone to nitrocellulose mole ratio is 1:1, i.e. when one molecule of CH_3COCH_3 corresponds to three ONO_2 groups.

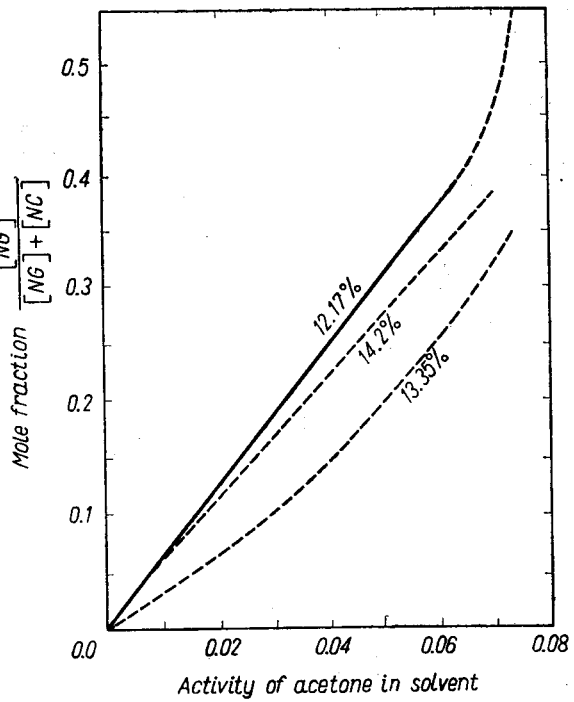
Miles [16] has reported similar results for nitrocellulose containing acetone absorbed from a water solution.

From these facts it seems beyond doubt that the crystal lattice of nitrocellulose undergoes a marked deformation as the result of absorbing a solvent or gelatinizer. For the time being it is difficult to say whether a new chemical compound is formed. Nevertheless the formation of molecular addition compounds appears likely. It is also without question that addition compound are formed by nitrocellulose and camphor. According to Hess *et al.* nitrocellulose of 13.7% N combines with camphor in a 1:1 mole ratio (one molecule camphor to one anhydroglucose unit).

The capacity of a nitrocellulose gel to bind solvents and gelatinizers should be considered as evidence that nitrocellulose yields addition compounds with those substances.



(a)



(b)

FIG. 94. Absorption isotherms of nitroglycerine (from chloroform solution) by nitrocelluloses, according to Desmaroux [46].

It is well-known in practice that about 1% of the solvent remaining in the nitrocellulose film can be removed only with difficulty. In the instance of a nitrocellulose film over 1% acetone is still retained after evaporating and drying at 70°C for 75 hr, as reported by Miles [16a].

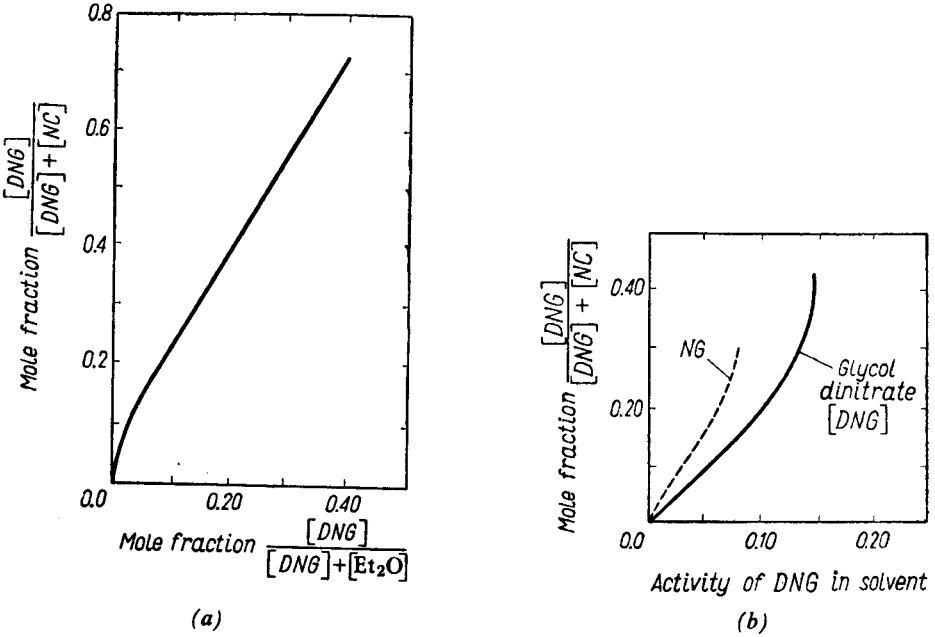


FIG. 95. Absorption isotherms of ethylene glycol dinitrate (from solution) by nitrocellulose of 12.2% N (Desmaroux [46]) as a function of concentration (a) and activity (b). Absorption of nitroglycerine (NG) is also given (b).

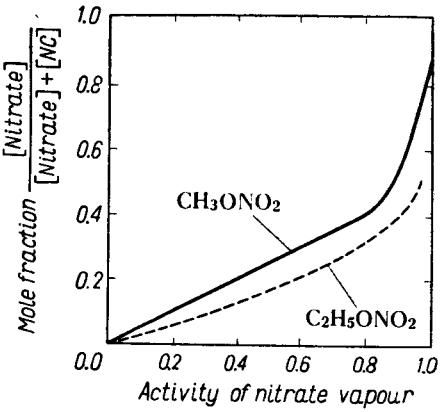


FIG. 96. Absorption of methyl and ethyl nitrates by nitrocellulose (12% N) from vapour at 40°C, according to Petitpas and Mathieu [27].

Data have been published by Baelz [48] concerning the retention of solvent by a 50 μ thick film dried at 25°C to a constant weight in air at 60% R.H. The results are shown in Fig. 97.

It is well-known that the camphor in celluloid is combined with nitrocellulose in such a stable manner that it is not removable by normal heating or evaporation under a reduced pressure.

As for the capacity of ether–alcohol to dissolve nitrocellulose, efforts have been

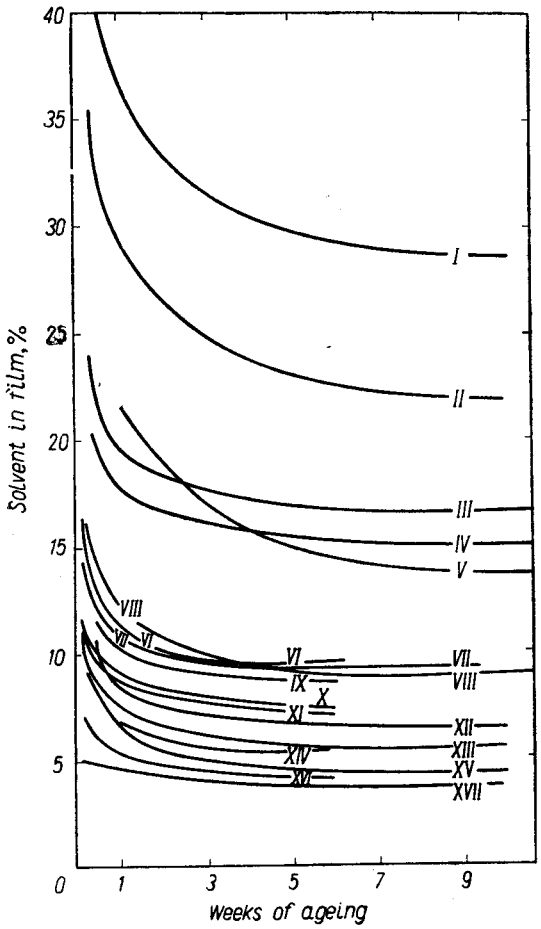


FIG. 97. Solvent retained by nitrocellulose films (50μ thickness) after exposure to air at 25°C (Baelz [48]). I—Cyclohexenyl acetate, II—methyl cyclohexanone, III—diacetone alcohol, IV—cyclohexanone, V—cellosolve acetate, VI—amyl acetate–ethyl alcohol 1 : 1, VII—amyl acetate, VIII—methyl cellosolve acetate, IX—amyl acetate–toluene 1 : 1, X—butyl acetate–ethyl alcohol 1 : 1, XI—butyl acetate, XII—cellosolve, XIII—methyl-ethyl ketone, XIV—cellosolve–toluene 1 : 1, XV—methyl cellosolve, XVI—ethyl acetate, XVII—acetone.

made to explain it by assuming that the alcohol forms molecular addition compounds with the ether, these in turn acting as solvents for nitrocellulose. Desmaroux and Vandoni [49] have established that ether forms molecular addition compounds with ethanol at mole ratios of 1:1, 1:3 and 1:5. However, the compounds are stable only in the neighbourhood of the freezing point of the mixtures, that is below

—100°C; at room temperature they undergo dissociation. Summing up it seems improbable that these compounds are of any importance in the dissolution process of nitrocellulose. The Highfield theory [36] (p. 248 and below) is more feasible.

General rule concerning nitrocellulose solvents. A number of suggestions for establishing a rule indicating which compounds are capable of dissolving nitrocellulose can be found in the literature. The best-known general rule is based on the principle that in order to dissolve a given substance a solvent of similar chemical constitution should be used. Thus, nitrocellulose being an ester, all esters can be used as solvents.

A more precise theory published by Highfield [36] has been mentioned already (p. 248). This author has drawn attention to the fact that having strongly polar (OH) groups and less polar (ONO_2) groups attached to a non-polar ring, nitrocellulose dissolves best either in liquids containing both polar and non-polar groups, for instance acetone, esters, acetic acid, or in a mixture of two liquids, one of which is polar, the other being non-polar or only weakly polar. As evidence supporting his view, Highfield reported that acetone mixed with 9% water is a better solvent of nitrocellulose (12.2% N) than acetone alone.

The influence of the polarity of solvents on their ability to dissolve nitrocellulose has been also demonstrated by Wo. Ostwald [50], who has introduced the value μ^2/ε as an expression characterizing the "strength" of solvent (μ—dipole moment, ε—dielectric constant). Good solvents of acetyl celluloses are characterized by a high μ^2/ε value. The physical significance of μ^2/ε is not clear, however, and its introduction has not helped to clarify the process of dissolution.

The solubility of high-nitrated cellulose (13.46% N) in a mixture of formic and acetic acid esters with ethyl alcohol was followed by T. Urbański [51]. The author established that for a range of homologous esters of both acids, the capacity of dissolving nitrocellulose increased in proportion with the value of the dipole moment of the ester. According to T. Urbański the sequence of formic acid esters corresponding with an increasing capacity to dissolve nitrocellulose is paralleled by the dipole moment values, as follows:

	μ
$HCOOCH_3$	1.21
$HCOOC_2H_5$	1.35
$HCOOC_3H_7$	1.50
HCOO-iso-C_4H_9	1.51
HCOO-iso-C_5H_{11}	1.60

Finally Papkov [52] observed that the surface tension of the solvent is a further factor influencing the solubility of cellulose esters. This worker established that the best solvents from a series of liquids resembling each other chemically, e.g. in a homologous range, were characterized by a moderate, "optimum" surface tension. Liquids having higher or lower surface tensions than this optimum value are worse solvents. The rule is also valid for mixtures. Thus a 50:50 acetone–water solution with a surface tension $\sigma = 30.4$ dyne/cm caused only a weak swelling of

nitrocellulose, whereas 75:25 acetone–water solution, having the surface tension $\sigma = 26.7$ dyne/cm, produced strong swelling.

Taking into consideration both the work of Ostwald, and that of Papkov, extended investigations into the ability of solvents to dissolve esters and ethers of cellulose have been carried out by Moll [53] who has linked the results of his experiments both with the electrostatic constants and with surface tension. The results of Moll's

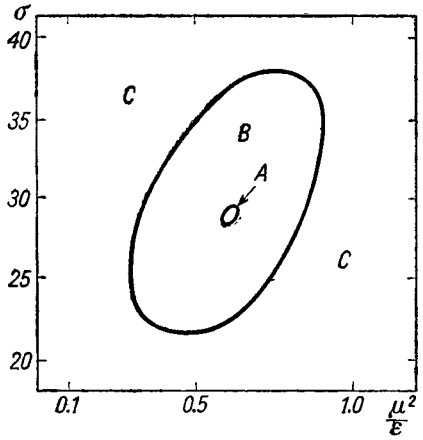


FIG. 98. Relation between μ^2/ε and surface tension σ of aliphatic liquids on their ability to dissolve cellulose trinitrate (Moll [53]).

investigations are described graphically, a typical example of his curves being shown in Fig. 98.

The graph concerns cellulose trinitrate and aliphatic solvents including alcohols, ketones, esters, nitroparaffins, chloroderivatives of hydrocarbons. The liquids are ranged in respect of their μ^2/ε values and of surface tension σ.

Liquids forming highly viscous solutions are characterized by constants included within the curve *A*. These are:

ethylene glycol acetate ($\mu^2/\varepsilon = 0.62$, $\sigma = 29.0$)
methoxybutanol acetate ($\mu^2/\varepsilon = 0.64$, $\sigma = 28.8$)

Other liquids capable of dissolving trinitrate give less viscous solutions. The constants μ^2/ε and σ for those substances are situated in an area enclosed by the curve *B*. Values of both constants that lie outside the curve *B*, in the area *C*, indicate solvents which are merely able to cause cellulose trinitrate to swell (Fig. 99).

The chart in Fig. 99 concerns liquid cyclic compounds (aromatic, hydroaromatic, heterocyclic). In this graph, the curve *B* limits the area characterizing liquids that produce solutions of relatively low viscosity while the area *C* again defines liquids that cause swelling only.

On the basis of many years' experience it has been established which groups of chemical compounds are capable of dissolving nitrocellulose:

(1) Alcohols: methyl, ethyl, propyl and other alcohols (in case of low-nitrated cellulose).
(2) Aldehydes: acetaldehyde, benzaldehyde, furfural.

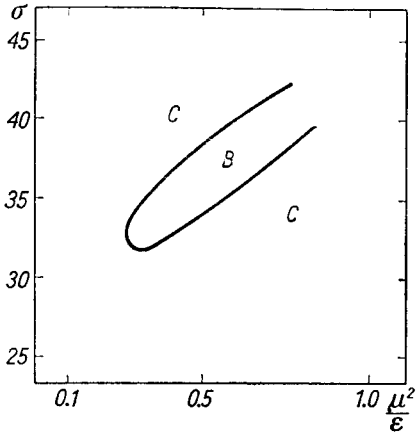


FIG. 99. Relation between μ^2/ε and surface tension σ of cyclic liquids on their ability to dissolve nitrocellulose (Moll [53]).

(3) Ketones: acetone, methyl ethyl ketone, propione, acetophenone, cyclohexanone, camphor.
(4) Ethers: methyl, ethyl, propyl, butyl etc. ethers in mixtures with alcohols.
(5) Inorganic acid esters: nitrates (e.g. methyl nitrate, nitroglycol, nitroglycerine), silicates (e.g. ethyl silicate), phosphates (e.g. triphenyl phosphate, tricresyl phosphate), mixed esters of nitric and hydrochloric acid (e.g. chlorohydrin dinitrate).
(6) Organic acid esters: carbonates (e.g. ethyl carbonate), formates, acetates (e.g. ethyl acetate, butyl acetate, amyl acetate), propionates, etc., oxalates (e.g. ethyl oxalate), maleates, phthalates (e.g. butyl phthalate); carbamates and phenylcarbamates (e.g. ethyl phenylcarbamate).
(7) N-substituted carbonamides: e.g. acetanilide, substituted urea-derivatives.
(8) Aliphatic nitro compounds: nitroparaffins (e.g. nitromethane, nitroethane, etc.).
(9) Aromatic nitro compounds: nitrobenzene, nitrotoluene, dinitrobenzene, dinitrotoluene, trinitrotoluene, nitroanisoles and nitrophenetoles, dinitroanisoles and dinitrophenetoles, nitrophenols etc.
(10) Heterocyclic compounds: pyridine, picolines (these substances cause nitrocellulose to denitrate), dimethylpyrone.

Solubility of nitrocellulose in ether–alcohol. In commercial practice, in the explosives industry, the most widely used solvent is a mixture of ether and alcohol. The solubility of nitrocellulose depends upon two factors: (1) the degree of polymerization of the nitrocellulose, (2) the nitrogen content of nitrocellulose. (1) The influence of the degree of polymerization on the solubility in ether–alcohol has not been investigated systematically, hence there exact information is lacking. However, from many years' observation in the manufacture and application of nitrocellulose is possible to take for granted the conclusion that the higher the molecular weight of the nitrocellulose the lower its solubility.

Nitrocellulose with a decreased molecular weight may be obtained as the result of depolymerization (degradation) of the cellulose before nitration, e.g. by keeping it at a temperature of 150–170°C or by treating it with acids. The resultant hydrocellulose, which usually possesses a lower molecular weight than cellulose, is then subjected to nitration to produce a more soluble substance as compared with the nitration product of a non-depolymerized raw material.

Further, the stabilization boiling of the nitrated cellulose exerts an express influence on the solubility of nitrocellulose. It causes the substance to become more soluble due to partial depolymerization and denitration. (A certain, insignificant decrease of nitrogen value occurs owing to partial hydrolysis). According to Bruley [54] the following relationship exists:

	solubility, %	nitrogen content, %
after 20 hr of boiling	5.2	12.99
after 60 hr of boiling	11.3	12.94
after 100 hr of boiling	10.9	12.95
after 140 hr of boiling	14.8	12.91
after 220 hr of boiling	21.2	12.94
after 260 hr of boiling	22.4	12.92

Likewise the solubility of nitrocellulose in ether–alcohol solution is improved by prolonged heating of the substance, accompanied by a reduction in the nitrogen content. Data from Lacape [55] show that nitrocellulose of 13.03% N and 7.0% of soluble matter, after being maintained at 108.5°C for 50 hr, has a nitrogen content of 12.65% and a solubility of 52.7%. On the other hand, nitrocellulose of 11.73% N, 98% soluble after being heated for 35 hr at 108.5°C was found to have a nitrogen content of 11.11% and its solubility fell to 92.7%.

The change of solubility in both of these instances occurs not only in consequence of depolymerization, but also owing to partial denitration.

(2) The influence of nitrogen content on the solubility of nitrocellulose in ether–alcohol has been known for a long time. Cellulose nitrates of an average nitrogen

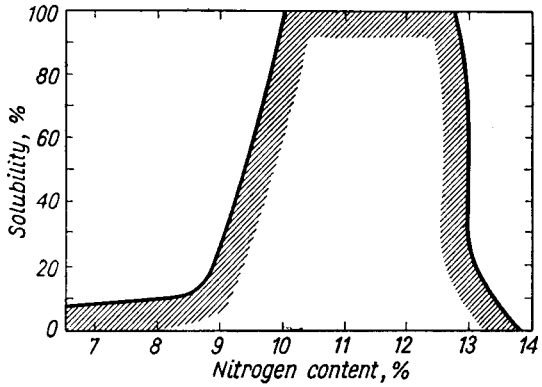


FIG. 100. Solubility of nitrocellulose in ether–alcohol against nitrogen content.

content from 10.5 to 12.2% dissolve in ether–alcohol, while nitrates containing more nitrogen (12.8–14.1%) or less than 10% are insoluble in mixtures of this kind. Some inclination towards higher or lower solubility is induced by the molecular dimensions, but the influence of this factor is rather limited.

The effect of nitrogen content on the solubility of nitrocellulose in ether–alcohol (2:1) is shown in the graph in Fig. 100.

This was found by several authors. One of the latest reports on the subject is given

by Trommel [55a]. He found that the solubility rapidly decreases as the nitrogen content increases from 12.9 to 13.15% N.

In his investigations into the relationship between the solubility of nitrocellulose and its nitrogen content Brunswig [55b] has claimed that the solubility is independent of the method of preparing nitrocellulose of a given nitrogen content — whether it was performed by direct esterification of cellulose, or by hydrolysing a higher nitrated cellulose with a mixture of dilute acids. By drowning nitrocellulose containing 13.2% of nitrogen, of 5% solubility in a sufficiently dilute acid mixture, the nitrogen content may be reduced to 12.6%. The solubility of the nitrocellulose thus obtained is 100%, exactly the same as that of nitrocellulose with the same nitrogen value produced by direct nitration of cellulose.

However, de Bruin and Witte [55c] found that the solubility of partly denitrated nitrocellulose is abnormal. Thus, nitrocelluloses of 13.43 and 12.98% N prepared by direct nitration had solubilities in ethanol–ether (1:2 by volume) of 5 and 100% respectively.

Nitrocellulose of the same nitrogen contents prepared by denitration had solubilities of 13 and 45% respectively.

The authors attribute this to the influence of the OH groups which in the denitrated product are not distributed randomly but are placed preferentially in such a way that the OH groups of neighbouring chains can be linked by hydrogen bonds.

The solubility of nitrocellulose depends to an appreciable extent on the conditions of nitration. Among several nitrocelluloses with roughly the same nitrogen

TABLE 42

THE SOLUBILITY OF NITROCELLULOSE IN ETHER–ALCOHOL

Water content of nitrating acid %	Nitrogen content of nitrocellulose %	Solubility %	Molecular weight of nitrocellulose (from viscosity measurements)
3.73	13.34	1.81	220,000
5.12	13.38	3.76	150,000
6.99	13.43	3.51	170,000
12.92	13.33	3.12	190,000
13.77	13.40	3.67	185,000
15.61	12.62	89.0	150,000
15.87	12.72	100.0	130,000
18.60	11.81	100.0	90,000
18.76	11.94	100.0	95,000
21.50	10.03	36.21	40,000
22.33	9.64	28.25	25,000

content (13.5–11.0% N) prepared by means of different nitrating acids the nitrocellulose with the highest solubility was the one made from the nitration mixture containing more water. Hence, in practice it is assumed that an increase of 1% in the water content of the mixed acids giving products of 13.4–12.0% N will cause the solubility of the nitrocellulose to increase considerably, while the nitrogen value is decreased only to an insignificant degree, e.g. 0.1–0.2%.

In Table 42 the effect of the water content of the mixed acid on the solubility of cellulose nitrates in ether–alcohol, mixed in a 4:3 weight ratio, taking into account also the molecular weight of the nitrocellulose, is shown according to Schiemann and Kühne [56]. (The figures also indicate the strong depolymerizing or degrading activity of water-rich nitrating acids.)

The composition of the solvent, i.e. the ether to ethyl alcohol ratio, also exerts an influence on the solubility of nitrocellulose. Gibson and McCall [57] found that the composition of ether–alcohol showing the highest solubilizing capacity differed according to the nitrogen value of the nitrocellulose. The ether–alcohol mixtures which are the best solvents for nitrocellulose of a given nitrogen content are as follows:

N content, %	the optimum volumetric ether to alcohol ratio
11.80	50:50
12.20	53:47
12.55	70:30

With solutions that have been prepared from solvents at a limiting ratio, i.e. where a small change in the proportion of the solvents may cause the dissolved nitrocellulose to coagulate, the highest viscosities are observed. The question is discussed below.

Solubility in alcohol and in other solvents. The solubility of nitrocellulose in alcohol is relatively low. In the case of nitrocellulose containing more than 11% of nitrogen the solubility in ethanol does not exceed a few per cent. Lower nitrated products are dissolved up to 100%, but further lowering the nitrogen value leads to a product that dissolves only with difficulty.

Acetone is not capable of dissolving nitrocelluloses of nitrogen value less than 10%. They can be dissolved in dilute aqueous NaOH.

In ethyl acetate and in other organic esters nitrocellulose containing 10% of N or more is completely soluble.

VISCOSITY

Viscosity, as well as solubility, is a most important characteristic for distinguishing various types of nitrocellulose. The determination of viscosity is of great theoretical importance, since it is used to study the degree of polymerization of nitrocellulose. In commercial practice viscosity frequently plays a decisive part, for it is used to assess suitability of nitrocellulose for specific purposes. Thus, in

the manufacture of blasting gelatine or varnishes a nitrocellulose with the appropriate viscosity is used to make the required products. Films, protective coatings or tubes and cords of smokeless powders should neither be brittle not too soft: properties which depend mainly on the viscosity of the nitrocellulose.

With regard to their viscosity, nitrocellulose solutions demonstrate the typical properties of lyophilic colloids. The action of pressure, temperature and concentration causes anomalies to appear indicating that these solutions deviate from the

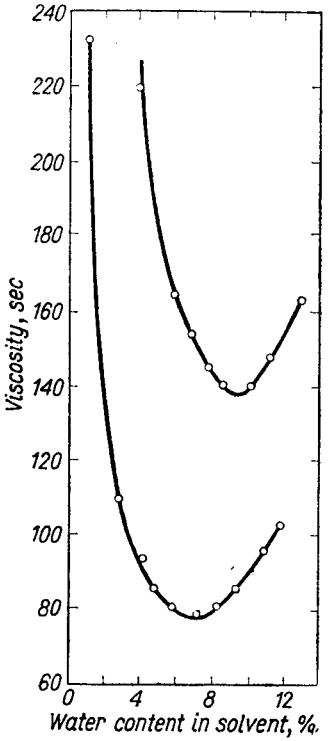


FIG. 101. Change of viscosity with addition of water to solutions of nitrocellulose in acetone (Masson and McCall [58]).

classical Hagen–Poiseuille's law of viscosity. The measurement of viscosity, as carried out in practice, is discussed on p. 277.

The viscosity of nitrocellulose solutions is to some extent dependent on the composition of the solvent, and on its solvent capacity or "strength". Masson and McCall [58] have examined the viscosity of nitrocellulose solutions in acetone to which different amounts of water had been added. They obtained a curve, reproduced in Fig. 101, that illustrates the effect of the water content of the acetone on the viscosity of nitrocellulose solutions.

The curve shows a distinct minimum viscosity at a water content of about 7%, since acetone containing this amount of water is a better solvent than anhydrous acetone. As the water content increases the dissolving "strength" of the solvent

is diminished. Simultaneously the viscosity of the solution increases. Finally, at a 12% water content the "limit of dissolution" is achieved, and on exceeding this percentage, precipitation of nitrocellulose gel takes place.

The viscosity of nitrocellulose solutions in ether–alcohol undergoes similar changes as the composition of the solvent is modified.

The relationship between the viscosity of 3, 4 and 5% solutions and the ether to alcohol ratios is outlined in the graph (Fig. 102) reproduced after Gibson and

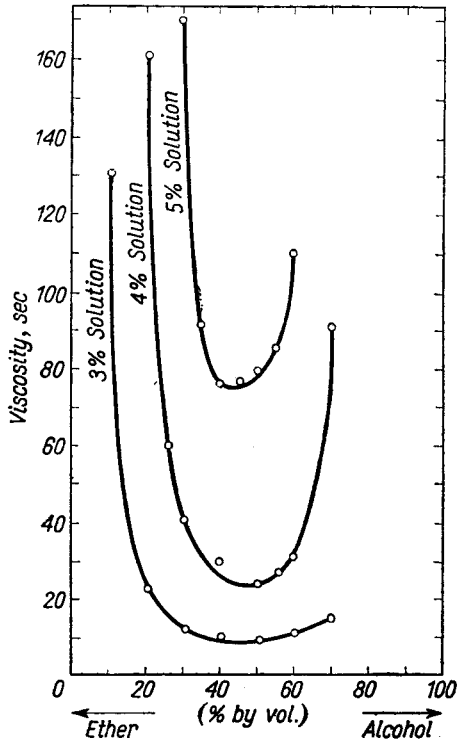


FIG. 102. Influence of the composition of the solvent (alcohol and ether) on the viscosity of nitrocellulose solutions (Gibson and McCall [57]).

McCall [57]. The minimum viscosity of a 4% solution corresponds to a mixture of 55 parts by volume of ether with 45 parts by volume of alcohol (1.1:1 parts by weight). A solvent composed of 75% of ether and 25% of ethanol produces a high viscosity solution. By an inappreciable decrease of the alcohol content the precipitation of nitrocellulose gel is brought about. The opposite effect, giving a high-viscosity solution on the border of gel precipitation is produced by a solvent made up from 25% ether and 75% alcohol. The gel precipitates on the addition of a small amount of alcohol.*

* The viscosity, expressed in seconds, represents the time needed by a steel sphere 0.793 ±0.001 cm dia., weighing 2.0385±0.0007 g, to fall through a 10 in. layer of solution contained in a tube 2.5 cm dia., 35.5 cm long at a temperature of 25°C.

The *intrinsic viscosity* $[\eta]$ (dl/g or ml/g) is an important physico-chemical constant of polymers estimated by extrapolation to an infinite dilution, that is to a zero concentration of the polymer. (For the Fikentscher function k — "Eigenviscosität" — see p. 278). If the intrinsic viscosity were in fact a measure of the length of the polymer chain molecules, then it would be expected not to vary as a result of changing the solvent. Dobry [59] has determined the viscosities of 0.04% solutions of nitrocellulose (11.4% N) in different solvents and calculated the intrinsic viscosity by means of extrapolation. The results are collected in Table 43. The changes in the

TABLE 43

THE INTRINSIC VISCOSITY OF NITROCELLULOSE

Solvent	$[\eta]$	Solvent	$[\eta]$
Acetic acid	0.33	Cyclohexanone	0.33
Acetone	0.29	Acetophenone + 3% of ethanol	0.32
Methyl cyanide	0.31	Ethyl benzoate + 11% of ethanol	0.32
Methanol	0.30	Methyl salicylate + 20% of methanol	0.33
Isobutyl formate	0.30		
Ethyl formate	0.32		
Nitrobenzene	0.32		

intrinsic viscosity brought about by varying the solvents are negligeable. Lindsley [60] has come to the same conclusion.

Nevertheless, such a uniformity in results has not been confirmed by all investigators. Thus G. G. Jones [61] has found a range of less uniform values for high-viscosity collodion nitrocotton HH, with 12.2% N. Some of these data are collected in Table 44.

TABLE 44

THE INTRINSIC VISCOSITY OF COLLODION COTTON

Solvent	$[\eta]$
Acetone	0.53
Methanol	0.53
Ethyl lactate	0.66
Epichlorohydrin	0.69
Benzyl acetate	0.71
Nitrobenzene	0.66

The addition of aromatic hydrocarbons to a nitrocellulose solution in amyl acetate produces an increase in the viscosity of the solutions, as shown in a diagram published by Drinberg [62] (Fig. 103).

Different plasticizers added to nitrocotton solutions can reduce their viscosity. Thus it has been established (Nisizava [63]) that the addition of camphor lowers

the viscosity of nitrocellulose solutions. The same effect was reported by Wolff and Rosen [64] for nitrocellulose solutions in butyl acetate, to which additions of tricresyl phosphate and dibutyl phthalate were made.

The results published by other authors, concerning similar systems, for instance the work of Kozlov and Kalashnikova [65] on the behaviour of nitrocellulose and

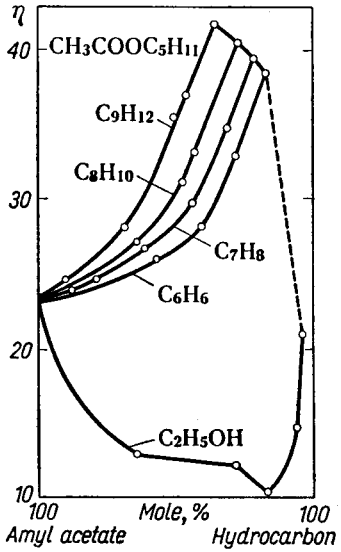


FIG. 103. Change of viscosity of nitrocellulose solution in amyl acetate with addition of aromatic hydrocarbons, according to Drinberg [62].

acetylcellulose in the presence of plasticizers, are inconsistent with the above observations. According to Kozlov and Kalashnikova on the addition of camphor or castor oil to an acetone solution of nitrocotton no change of viscosity occurred.

It is very interesting to observe the influence of aldehydes on nitrocellulose solutions. This has been done by Kozlov and Bedushevskaya [66]. This effect is most complicated, since in accordance with the said authors two processes were occurring simultaneously: the formation of cross links which produced an increase of viscosity, and a degradation of the long-chain molecules which reduced the viscosity.

An addition of diphenylamine causes a marked decrease in viscosity, as reported by Drinberg [62]. The viscosity of high-viscosity nitrocotton solution is decreased under the influence of a 5% admixture of diphenylamine (by weight of nitrocellulose) as much as 24%.

According to the work of Kozlov *et al.* [67] the viscosity of a 2% nitrocellulose (11.5% N) solution in acetone is decreased as a result of adding such electrolytes as lithium chloride up to a quantity equivalent to the number of available hydroxyl groups. The viscosity fell from 0.17 P to some 0.14–0.11 P.

When the amount of added lithium chloride was increased to a value equivalent to all the hydroxyl groups, both free and esterified, the viscosity was reduced to

0.0038 P. The change of viscosity is not brought about by any change of molecular weight, as this undergoes no diminution after treatment with LiCl.

The problems of the increase in viscosity of nitrocotton and the precipitating gel in the presence of inorganic compounds, owing to the formation of complex compounds, is discussed later (see p. 302).

The effect of temperature on the viscosity of nitrocellulose solutions has been studied by many authors, e.g. Nishida [68], Drinberg [62], E. Karrer *et al.* [69], Kozlov [70] and Goldman [71]. These experiments showed that the viscosity of concentrated nitrocellulose solutions is lowered more quickly, the higher the concentration of the solution. Attempts were made by E. Karrer, Berl and Umstätter [69] to find a formula expressing the relationship between the viscosity and the temperature (from 20 to 48°C). Shor [72] has examined the viscosity of nitrocellulose solutions within the concentrations range 14.9–17.9% and at temperatures from 0 to 40°C. On the basis of a mathematical analysis of the numerical results, the author has deduced the following formula:

$$\eta_t = \eta_0 e^{-kt}$$

where: η_t is the viscosity of the solution at a temperature t°C, η_0 is the viscosity of the solution at 0°C and k is a constant equal to about 0.05.

The determination of viscosity at 0°C is difficult to carry out, hence the author has modified his formula as follows:

$$\eta_t = \eta_{20} e^{1-0.05t}$$

where η_{20} represents the viscosity at 20°C.

Hence the formula for the temperature gradient is: $\frac{d\eta_t}{dt} = -0.05\eta_t$. Thus a change of the temperature of solution by 1°C causes the viscosity to vary by 5%. The equation has been confirmed by experiment. In the graph (Fig. 104) the calculated values fit well with the experimental data.

Ageing of nitrocellulose solutions. The tendency of nitrocellulose solutions to undergo changes in the course of time (to "age") has been known for many years. It consists mainly in a decrease of viscosity during the first ten to twenty hours after dissolution. At room temperature the decrease of viscosity stops after 1–2 days. At an elevated temperature it continues, and the viscosity approaches a certain asymptotic limiting value, that may be estimated by means of extrapolation.

The rate of decrease in viscosity, and the value of the lower limit at which the viscosity becomes stable depends on the type of nitrocellulose and on the solvent used. The higher the initial viscosity, the faster viscosity falls. However, the viscosity curves as a function of time never cross one another.

The reason why the viscosity falls is the effect of the solvent on the molecules of nitrocotton which tends to degrade the chains. The shortening of the molecular chains is relatively more marked in the case of long chains, i.e. with nitrocellulose

that produces the more viscous solutions. This is an irreversible process. If from a solution that is already stabilized in respect of viscosity, nitrocellulose is precipitated and then redissolved, then the viscosity of the new solution is exactly the same as immediately before the precipitation. Addition of acids or bases to the solution hastens the degradation of nitrocellulose.

Studying this phenomenon of ageing the viscosity measurements of the nitrocellulose must always be carried out at a pre-determined time, e.g. 24 hr, after the

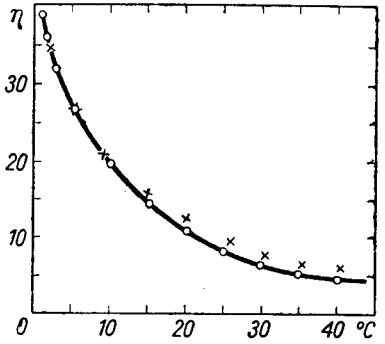


FIG. 104. Change of viscosity of nitrocellulose solution with temperature (○ —experimental and + — calculated values), according to Shor [72].

solution has been prepared and kept at room temperature, since otherwise the results obtained are not comparable.

Effect of storage on viscosity. Factors such as the method of storing undissolved nitrocellulose affect the viscosity of its solutions. It has been established (Kanamaru [73]) that nitrocellulose kept in a polar liquid, e.g. water, alcohol, and tested for viscosity at stated periods by dissolving samples in acetone, shows for the first few days a rather rapid increase in viscosity, which gradually becomes slower. If cellulose is stored in a non-polar liquid, such as carbon tetrachloride, or petroleum ether, then the viscosity of solutions remains unchanged or increases only very slightly.

From samples examined by means of X-rays it has been established that the increase in viscosity is related to an improved orientation of the microcrystals along parallel axes.

Effect of the degree of polymerization on the viscosity. It has been made clear by the experiments of many authors that operations leading to the degradation of cellulose prior to nitration contributes to the production of a less viscous nitrocellulose. Moreover, the degree of polymerization of cellulose before nitrating depends upon the origin of the cellulose: the type of plant, its age and so on. The properties of the cellulose, such as polymerization degree, are passed on to the nitrocellulose, as already stressed (p. 246), to exert an influence on the viscosity of the product. Hence cotton yields nitrocellulose solutions more viscous than these from wood

pulp cellulose and the solutions of the product from long fibre cellulose are more viscous than those from short fibre cellulose. Solutions prepared from nitrocellulose of older plants demonstrate a lower viscosity.

The relationship between the viscosity of nitrocellulose solutions and the age of poplar wood cellulose according to Pascal [74], is shown in Table 45.

TABLE 45

THE EFFECT OF THE AGE OF WOOD ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Age of poplar years	Nitrogen content %	Viscosity sec
26–48	10.5	128
24–36	10.9	201
8–24	10.9	248
8	10.8	697

As shown experimentally by Piest [75], cotton which was subjected to various operations, e.g. bleaching, treatment with alkalis or acids, strong heating prior to nitration furnishes nitrocellulose solutions of low viscosity. At the same time an increase in the solubility of the nitrocotton was also observed. This is evidence that the cellulose molecules are shortened and their content of terminal group is increased. A certain proportion of hydrocellulose and oxycellulose may result. The total effect is to bring about an increase in the reductive properties of the cellulose, i.e. an increase of the copper number.

In Tables 46 and 47 results reported by Gabillon [76] are tabulated.

TABLE 46

THE EFFECT OF HEAT TREATMENT OF CELLULOSE ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Cotton	Copper number	Nitrogen content %	Viscosity sec	Solubility in alcohol %
Without heating	0.25–0.27	11.82	480	3.6
Heated for 4 hr at 120°C	0.28–0.30	11.90	320	3.9
Heated for 8 hr at 120°C	0.26–0.34	11.90	270	3.5
Heated for 12 hr at 120°C	0.32–0.39	11.94	238	5.8
Heated for 4 hr at 130°C	0.31–0.37	11.92	350	5.6
Heated for 8 hr at 130°C	0.40–0.43	11.95	276	6.7

Effect of the conditions of nitration. The conditions under which the nitration was carried out exert an appreciable influence on the viscosity of nitrocellulose solutions. Thus a high nitrating temperature produces low viscosity nitrocellulose

TABLE 47

THE EFFECT OF CHEMICAL TREATMENT OF CELLULOSE ON THE PROPERTIES AND YIELD OF NITROCELLULOSE

Cotton	Copper number	Nitrogen content %	Viscosity sec	Solubility in hot alcohol %	Yield %
No treatment	0.26–0.29	12.22	78	3.1	137
Treated with caustic soda under pressure	0.44–0.41	12.08	28	10.8	125
No treatment	0.13	12.06	730–810	0.95	150
Treated with 1% hydrochloric acid at 70°C	0.57	12.03	245–250	3.9	147.5
Treated in the same way at 80°C	0.96	12.03	39–40	11.09	140

since nitration at an elevated temperature is accompanied by degradation, hydrolysis, and oxidation processes to a larger extent than at a lower temperature.

The following relationship has been given by Berl and Klaye [77]:

nitrating temperature, °C	viscosity, sec
25	1215
35	765
45	480

An exactly similar decline of viscosity is observed, according to Gabillon, on raising the temperature to 45°C. The effect of nitration at a temperature exceeding 45°C (45–65°C) produces a considerably smaller diminution though the decrease in yield is appreciable. Data quoted by Stark [78] for cotton nitrated for 30 min by means of a mixed acid composed of

38.5%	HNO_3
44.5%	H_2SO_4
17.0%	H_2O

are given in Table 48.

TABLE 48

THE INFLUENCE OF NITRATION TEMPERATURE OF CELLULOSE ON THE VISCOSITY AND SOLUBILITY OF NITROCELLULOSE SOLUTIONS

Nitration temperature °C	Nitrogen content %	Viscosity sec	Solubility in ether–alcohol %
15	10.7	330	52
18	10.9	280	68
20	10.8	260	79
22	11.2	205–290	84–98
40	11.5	28	100

Prolonged nitration favours the processes of degradation and oxidation, and hence also the reduction of viscosity. Schur and Hoos [78a] have nitrated wood pulp cellulose at various temperatures to attain results as follows (Table 49).

TABLE 49

THE TEMPERATURE OF NITRATION AND THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Temperature °C	Nitrogen content %	Viscosity sec	Yield %
40	11.09–11.19	50–80	150.7–155.2
45	11.13–11.31	15–27	146.8–150.0
50	11.25–11.35	11–14	136.5–147.2
55	11.41–11.44	5–6	125.5–134.0

In the Table 50 data have been collected from the investigation of the influence of the time of nitration by means of a mixed acid composed of:

38.2%	HNO_3
44.5%	H_2SO_4
17.3%	H_2O

at 22°C, on the viscosity of nitrocellulose solutions.

TABLE 50

THE EFFECT OF TIME OF NITRATING CELLULOSE ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Time of nitration min	Nitrogen content %	Viscosity sec	Solubility in ether–alcohol %
30	11.8	180	99.3
35	12	160	99.5
40	12	138	99.7
45	11.9	102	99.3
60	11.8	93	98.5

An increase of the nitrogen content is also accompanied by an increase of viscosity, providing that the nitrocotton is prepared under accurately uniform conditions. This relationship is described by Berl and Klaye [77] as tabulated below (Table 51).

In these experiments the nitrocellulose was washed (free of acid) with cold water only after being nitrated.

TABLE 51
THE RELATIONSHIP BETWEEN THE NITROGEN CONTENT AND VISCOSITY OF NITROCELLULOSE

Nitrogen content %	Viscosity sec
9.09	447
10.41	1800
12.48	16,200
13.02	18,600
13.50	322,500

It has been demonstrated in experiments by many authors that the nitrogen content has a distinct influence on the viscosity of solutions when identical conditions of nitration and purification of the nitrocellulose are used. Thus for a nitrocellulose containing 11.96% N, giving a solution of viscosity 203 sec, the molecules of nitrocellulose do not differ in chain length from those of a nitrocellulose containing 11.05% N giving a solution of only 27 sec viscosity (Krüger [79]). The molecular weight was determined by the diffusion method. Additional nitration of a lower nitrated cellulose yielded a more viscous product.

Of all the factors influencing viscosity the most important is the molecular weight of the raw material.

Okada [80] therefore suggested determining the molecular weight of cellulose by determining the viscosity of nitrocellulose derived from it. He suggested nitrating cellulose with a strong nitrating mixture (27.5% HNO_3, 63% H_2SO_4, 9.5% H_2O) and at low temperature (0°C) to yield a high nitrated product (13.0–13.2% N).

However, the conditions of nitration did not guard sufficiently against degradation, and oxidation (e.g. [146]), and a number of authors suggested nitration under conditions where the possibility of degradation and oxidation was considerably reduced. This is discussed on p. 343.

Thus Rogovin and Shlakhover [81] performed a stepwise nitration applying mixed acids composed of nitric acid, acetic anhydride and acetic acid. Nitrating mixtures of this composition do not bring about degradation, hydrolysis or oxidation of nitrocellulose during the nitration (see p. 344). Each additional nitration causes an increase of viscosity. The results are collected in Table 52.

In order to avoid the degradation of cellulose Wannow [82] used a mixture of nitric acid with phosphoric acid and water at temperatures of 0 and 20°C. The constant degree of polymerization was demonstrated by measuring the osmotic pressure. It has been confirmed that the viscosity of nitrocellulose solutions depends upon the nitrogen content of the substance (Fig. 105).

The extent to which the composition of the mixed acid influenced the viscosity of the nitrocellulose was followed by Berl and Berkenfeld [83]. They demonstrated that enriching the nitrating mixtures with sulphuric acid caused a considerable decrease in the viscosity of the nitrocellulose solutions.

TABLE 52

THE EFFECT OF AN ADDITIVE NITRATION ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Type of substance	Nitrogen content %	Viscosity	
		absolute, of a 2% solution in acetone sec	specific, of a 0.25% solution in acetone sec
Cellulose nitrate	11.40	93	0.78
Re-nitrated cellulose nitrate	13.39	348	1.75
Cellulose nitrate	11.28	186	0.95–1.0
Cellulose nitrate re-nitrated once	12.40	510	1.30
Cellulose nitrate re-nitrated twice	13.40	910	2.85
Cellulose nitrate	11.21	51	0.6
Re-nitrated cellulose nitrate	13.41	153	1.4

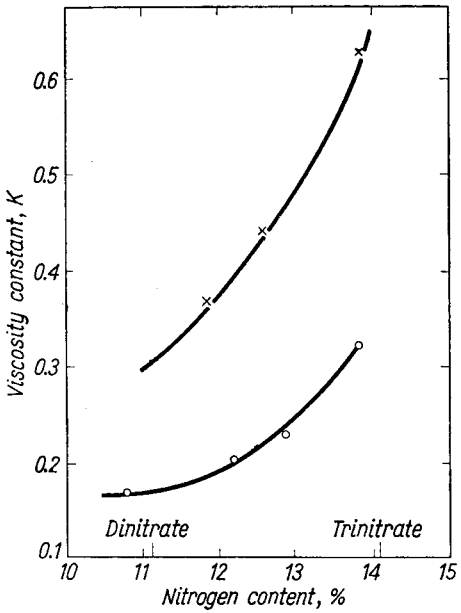


FIG. 105. Change of viscosity of nitrocellulose solutions with nitrogen content (Wannow [82]). + — Nitration at 0°C, ○ — at 20°C.

Effect of the treatment after nitration. The treatment of the nitrocellulose after nitration also exerts a major influence on the viscosity. Thus, for instance vigorous stabilization boiling leads to a decrease in viscosity. Values reported by Bruley [54] are given below:

boiling period, hr	viscosity, sec
10	703
14	454
18	424
24	389
32	279
40	254
48	237
60	140

A particularly marked change in the viscosity of nitrocellulose results from keeping it boiling in solutions of different reagents — bases and acids. In order to lower the viscosity of nitrocellulose, careful boiling in an alkaline medium is sometimes applied in practice.

Lenze, Metz and Rubens [84] reported the data assembled in Table 53.

TABLE 53

THE EFFECT OF AFTER TREATMENT WITH ALKALIS ON THE VISCOSITY OF NITROCELLULOSE SOLUTIONS

Treatment of nitrocellulose	Nitrogen content %	Viscosity of ether–alcohol solution sec	Solubility in 95% alcohol %	Copper number after denitration
Nitrocellulose untreated with alkalis	12.22	88	5.5	3.94
Nitrocellulose slightly treated with alkalis	12.18	64	5.4	4.06
Nitrocellulose treated slightly more with alkalis	12.16	29	9.2	5.71
Nitrocellulose treated strongly with alkalis	12.08	11.4	13.2	8.70
Nitrocellulose vigorously treated with alkalis	11.91	8	20.0	9.25

In view of the increase of the copper number it may be concluded that the substance undergoes strong hydrolysis and oxidation in the course of the treatment with alkali. Operations of this kind should therefore be performed with great care, since the over intensive action of these reagents and the appreciable fall in viscosity that ensues cause the gel formed after evaporation of the solvent to become brittle. In recent times therefore stabilization boiling under pressure has been widely applied.

The first references to this method were however published as early as 1899 (Schulz [85]).

Stabilization by boiling under pressure is now used:

(1) in order to shorten considerably the time of stabilization, which is usually the longest manufacturing operation;

(2) in order to attain the viscosity characterizing the collodion cotton intended for varnish making.

Various kinds of varnish collodion cotton differ widely in the viscosity of their solutions; ranging from an insignificant value to a high viscosity, achieved chiefly by means of stabilization boiling in an autoclave.

Wehr [86] reported the values tabulated below characterizing the change in viscosity brought about by keeping nitrocellulose boiling under pressure in water at 134°C (Table 54).

TABLE 54

Type of nitrocellulose	Nitrogen content %	Time of boiling at 134°C min	Intrinsic viscosity η
original	12.12	—	1.220
I	12.01	15	0.360
II	12.02	40	0.190
III	11.98	90	0.100
IV	11.98	165	0.050
V	11.97	295	0.029
IV	11.87	430	0.021

The viscosity of nitrocellulose is also affected by prolonged exposure to sunshine primarily by ultra-violet rays. It is beyond question that these cause shortening of the molecular chain. (Donald [87], Fric [88], Breguet and Caille [89], Stark [78] and others).

time of exposure to light, hr	viscosity, sec
—	335
24	320
48	305
480	270
900	240

Similar results due to irradiation were also established by Rogovin and Glasman [90]. Clément, Rivière and Beck [91] found that under the influence of the light only the viscosity of high-viscosity nitrocellulose was decreased, low-viscosity nitrocellulose did not undergo any change. In view of the experiments of Minc [92], quoted below, this observation appears to be inaccurate. Clément, Rivière and Beck observed, moreover, that the solubility was increased by irradiation. The increase of solubility may be brought about to some extent by a certain denitration

that accompanies the irradiation of nitrocellulose. Denitration produced by the influence of ultra-violet rays has also been reported by other workers (see p. 312).

As shown by Minc [92], the reduction in viscosity of collodion cotton, nitrogen content 11.2% N, dissolved in acetone by ultra-violet irradiation is greater, the higher the concentration of nitrocellulose in the solution.

Thus in the instance of 1% solution exposed for an interval of 4 hr to the action of light the decrease in viscosity is 0.3–0.7%. With 10–20% solutions, on the other hand, the reduction in viscosity during the same period is 25.0–34.2%. Minc's experiments showed that in solutions of low viscosity the reduction of viscosity could remain unobserved. Claesson and Wettermark [92a] investigated the irradiation of solutions of cellulose nitrate with light of wave-length 253 mμ. The depolymerization was followed viscosimetrically and the chain breakage was found to obey the course predicted theoretically for a random process with a quantum yield of 0.01–0.02.

In their more recent paper Claesson, Palm and Wettermark [92b] investigated the magnitude of the degradation of nitrocellulose (12.2% N)

(1) at different wave-lengths,

(2) when the energy of the light was varied.

A solution of nitrocellulose in methanol (concentration 0.40–0.45%) showed depolymerization after exposure to light to the wave-length 302 mμ, whereas no depolymerization was detectable after exposure to the wave-lengths 334 and 365 mμ. Solutions of the same nitrocellulose sensitized by adding *ca.* 1% β-naphthylamine showed depolymerization at all the wave-lengths.

The viscosity of the solutions fell from $[\eta] = 4.14$ to *ca.* 2.4 dl/g during the first 50 hr exposure, after which it rapidly assumed a constant value. The decomposition of nitrocellulose by light is discussed later (see p. 312).

Ultrasonic waves also bring about a reduction in the viscosity of nitrocellulose. The effect is more marked the higher the initial viscosity, and thus the longer the nitrocellulose chains (Sollner [93]; Schmidt and Rommel [94]). For instance, nitrocellulose with a molecular weight of 123,000, estimated by means of Staudinger's viscosity equation, subjected in solution form to the action of ultrasonic waves suffered a degradation to a molecular weight of 70,000–80,000.

In more recent experiments, Edelmann [95] has followed the depolymerization of nitrocellulose in dilute (0.5%) solution. He reported that nitrocellulose of an average polymerization degree $n = 1060$, and containing considerably amounts of the $n > 2500$ fraction, was degraded after being subjected for 1 and 4 hr to the action of ultrasonic waves of 800 kc/sec to an average polymerization degree of $n = 910$ and 630 respectively. By fractionation, the presence of a small quantity of $n = 1400$ was established in the latter.

The action of ultrasonic waves seems likely to be the result of mechanical rupture of the long chain molecules of nitrocellulose on being rubbed by the violently oscillating particles of solvent. Thus it is one of rare examples of depolymerization brought about by mechanical forces. Further evidence in favour of the supposition that mechanical forces may cause the substance to depolymerize is provided by the

effect of pulping nitrocellulose in beaters on the viscosity of the product. The shortening the nitrocellulose fibres that occurs reduces its viscosity. According to Bruley [54] the relation can be depicted numerically, as shown in Table 55.

TABLE 55

THE EFFECT OF BEATING NITROCELLULOSE ON THE VISCOSITY OF ITS SOLUTION

Viscosity, sec	
before beating	after beating
109	82
228	117
92	50
89	53

More recently Staudinger and Dreher [96] have confirmed these observations, by determining the effect of the time of pulping nitrocellulose in a colloid mill on its molecular weight as determined by viscosity measurement. They further established that owing to intensive milling a partial denitration of nitrocellulose took also place, as seen in Table 56.

TABLE 56

THE RELATION BETWEEN THE TIME OF BEATING NITROCELLULOSE AND ITS MOLECULAR WEIGHT

Time of beating, hr	% N	Molecular weight
0	12.95	430,000
4	12.80	125,000
8	12.46	80,000
12	11.75	47,000

Recently, the effect on the nitration product of beating the cellulose prior to nitration has been studied by Ellefsen [97] who confirmed the well-known view that beating of cellulose was accompanied by partial degradation to soluble substances. However, the molecular weight was unchanged in those fractions of cellulose that did not dissolve in water.

Sometimes an increase in the viscosity of nitrocellulose is possible, through cross links formed between free hydroxyl groups. This involves the chemical reactions of cellulose, which are discussed later (see p. 303).

It follows from the experiments of Nishida [98] and Kozlov [70] that mixing or stirring solutions of nitrocellulose causes the viscosity to increase initially and then to fall. As mentioned already (p. 261) the viscosity of nitrocellulose is of major

importance for the properties of smokeless powder gel. Low viscosity solutions yield a brittle gel. Besides, the lower the viscosity the more the gel shrinks on removal of the solvent. More detailed information regarding the relationship between the viscosity of nitrocellulose and its suitability for use in powder manufacture is contained in Vol. III.

The viscosity of commercial types of nitrocellulose is tested by means of a variety of different methods in various countries.

The Ardeer Method is the most commonly used in Great Britain and in the British Commonwealth [16a]. The determinations are made in acetone of specific gravity 0.8097 at 20°C, prepared by mixing 95.0 volumes of acetone and 5.0 volumes of water, by the falling-sphere method adapted in the first place for military nitrocelluloses by Masson and McCall [58]. As mentioned already (p. 262) these authors found that the addition of a small amount of water to the acetone reduced the viscosity of the nitrocellulose solution very considerably and that a minimum viscosity was reached with a certain percentage of water, which varies from one nitrocotton to another (Fig. 101). The apparatus is calibrated with sugar solution of known absolute viscosity. The results are calculated on the assumption of specific gravity of 0.80 for all nitrocellulose solutions and are always reported in c.g.s. units (poises, P) at 20°C. The viscosity figure is always preceded by one of the following letters: X, L, M or H, which in the usual I.C.I. dual notation, indicate different ranges of both nitrogen content and viscosity. First letter (N-content): L = 10.5–11.2%, M = 11.2–11.8%, H = 11.8–12.2%. Second letter (viscosity): X = lowest, H = highest. A general idea of the viscosity range can be gathered from the concentrations quoted, for each of which a steel ball 1/16 in. in diameter has to fall through 15 cm of the solution within a period of 6 sec to 6 min. The time of fall on seconds is approximately twice the viscosity in c.g.s. units.

There are four degrees of viscosity: X, L, M, and H. In each a different concentration is used, thus for X, L, M and H the concentrations are 40, 20, 10 and 3% respectively (in g per 100 ml solvent). These ranges bear no simple relation to each other, and the general use of conversion factors to convert a viscosity determined in one range into another is quite inadmissible.

Many other formulations are in use. The most general in the United States is the Hercules Method [16a]. Determinations are also made at various concentrations, but the solvent consists of ethyl acetate, ethyl alcohol, and toluene in the proportions 20:25:55 by weight. Results are recorded in c.g.s. units, as in the Ardeer Method, but at the same time a general classification of nitrocelluloses as e.g. "5 sec", "1 sec", "½ sec" -product and so on is in use. These are the times of fall of a steel ball through a 10 in. layer of solution containing 12 g nitrocellulose in 100 g of solution. The smallest are derived by extrapolation from data obtained with more concentrated solutions and are fictitious. Thus commercial sorts of nitrocotton furnished by the Hercules Powder Co. possess viscosities corresponding to the following values: 1/4, 1/2, 15–20, 25–30, 30–40, 60–80 and 125–175 sec. Products used for varnish making possess the first four viscosities.

Viscosity determinations at the highest convenient concentration are of practical value, because in most of the applications of nitrocellulose, solutions of these concentrations are used, and there is usually little difference between the concentration in use and that used for the determination. All nitrocellulose solutions that are not very dilute show more or less abnormal viscosity, i.e. the rate of flow is not proportional to the applied stress or pressure. The ease of flow of a solution at one degree of stress cannot then be inferred from a "viscosity" determined at another. Nevertheless the measured viscosity of a comparatively concentrated solution is in general useful information. This advantage is sacrificed in what is the most rational of all viscosity systems, the German I.G. Method. Measurements are made in dilute solutions and the results are expressed in terms of the "Eigenviscosität" (k) of Fikentscher and Mark [99] a function which to a large extent is independent of concentration:

The Fikentscher function k can be defined by means of the expression:

$$\ln \eta_r = \frac{75k^2c}{1+1.5kc} + kc$$

c being the concentration in g/ml.

The values accepted are those of the Fikentscher k multiplied by 10,000. This system, which specifies the nitrocellulose and not its solutions, is the most scientific and consistent of all, but is limited to German practice only. For example, E510 and E950 I.G. nitrocelluloses correspond to $\frac{1}{2}$–1 and 12.5 sec Hercules and X39–X140 and L125 Ardeer products respectively.

FRACTIONATION OF NITROCELLULOSE

Long ago it has been established that nitrocellulose is not a homogeneous substance. The earliest experiments in this field were made by Stepanov [100] who used the method of fractional precipitation from an acetone solution by the addition of water. Stepanov added different amounts of water stepwise to a solution of nitrocellulose in acetone to obtain fractions varying slightly, corresponding with the nitrogen content. The first and least soluble fraction contained 13.15% of nitrogen, while the N-content of the last, fifth portion, was 12.90%.

Duclaux *et al.* [101] came to other conclusions for he established that particular fractions differed only in the viscosity of solutions the nitrogen content being the same. In order to precipitate nitrocotton from its acetone solutions the authors added acetone–water mixtures, richer and richer in water until finally pure water was added. A range of fractions was separated from nitrocellulose acetone solution of viscosity 0.1 P (poises). The viscosity of the first fraction was 0.603 P, and that of the last 0.007 P (2% solutions).

Identical results of fractionating nitrocellulose by successive dissolution and precipitation have also been reported by other authors, e.g. Brunswig [102] Kumichel [103], Lacape [55], Glikman [104].

The most extensive investigations were those of Medvedev [105]. Commercial collodion cotton of 11.08% N was divided by Medvedev into four fractions. The viscosity of the acetone solutions as well as the molecular weight (osmotic method) of these were determined. The nitrogen content in all the fractions was approximately the same (Table 57).

TABLE 57

THE PROPERTIES OF COLLODION COTTON FRACTIONS

Fraction	Nitrogen content %	Specfic viscosity of solution of concentration:			Molecular weight (by osmotic pressure)
		2%	1%	0.25%	
I	11.4	21.56	3.9	0.39	25,000
II		26.37	4.67	0.43	60,000
III	*ca.* 11.8	24.52	4.47	0.42	40,000
IV		57.50	7.30	0.68	75,000

Lipatova and Lipatov [106] also found that the fractions of higher viscosity possessed a higher temperature coefficient of viscosity.

In other experiments, the opposite method of fractionation by dissolution was applied. In this way G. Meissner [107] prepared a soluble fraction with a nitrogen content of 10.28%, in quantity about 4% by extracting a specimen of nitrocellulose with 12.17% N using 50:50 ether–alcohol. The insoluble part was composed of nitrocellulose of 12.32% N.

Nitrocellulose has also been extracted with alcohol, the residue then being treated with a mixture of ether and ethanol (60:40 by volume, Berl and Hefter [108]). Three fractions were isolated: the *first* soluble in alcohol, the *second* soluble in ether–alcohol, and the *third* an insoluble residue. The fractions differed in nitrogen content. The lowest nitrogen content was found in the first fraction and the highest in the third fraction (Table 58).

TABLE 58

THE PROPERTIES OF NITROCELLULOSE FRACTIONS

Nitrogen content of original nitrocellulose	Solubility, %		Nitrogen content of fractions, %		
	in alcohol	in ether–alcohol	(1)	(2)	(3)
12.65	7.44	92.40	9.6	12.60	12.25
13.13	2.68	8.60	9.7	12.15	13.35
13.17	2.40	11.43	—	12.00	13.15
12.72	2.80	74.00	—	12.96	13.00

Similarly Craik and Miles [109] extracted nitrocotton by means of aqueous acetone with a gradually increasing acetone concentration. The fraction which

dissolved with the greatest facility was the poorest in nitrogen, whilst the insoluble portion contained more nitrogen than the original substance. These workers also studied the viscosity of the fractions, finding that the less soluble fractions yielded the more viscous solutions.

A range of nitrocotton samples containing from 11.3 to 13.1% N, and nitroramie of 10% N prepared by denitrating nitroramie of 13% N by acting with nitric acid 80%, have been fractionated by G. G. Jones and Miles [110] by a method of successive extraction with aqueous acetone: every subsequent solvent was richer in acetone than the preceding one. They demonstrated that particular fractions differed in nitrogen content and viscosity.

The change of nitrogen content as the extraction proceeded is showed in Fig. 106. From their collected results Jones and Miles have constructed a graph (Fig. 107)

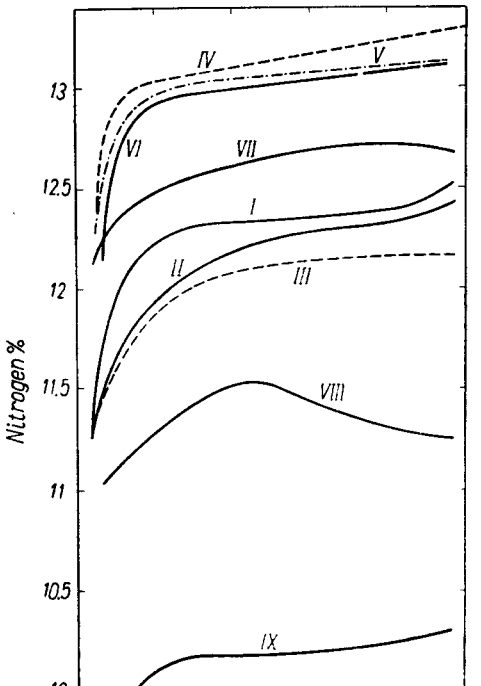


FIG. 106. Nitrogen contents of extracted nitrocellulose fractions according to G. G. Jones and Miles [16a]: (I) HH nitrocellulose, 12.20% N, high viscosity, unkiered; (II) HX nitrocellulose, 12.26% N, low viscosity; (III) HX nitrocellulose, 12.07% N, low viscosity; (IV) Guncotton, unkiered, 13.14% N; (V) Guncotton, kiered, 12.95% N; (VI) Guncotton, kiered, 12.93% N; (VII) "Pyro" nitrocellulose, 12.70% N; (VIII) Nitro-woodpulp, 11.30% N; (IX) Nitroramie (73.5% soluble in acetone), 10.00% N.

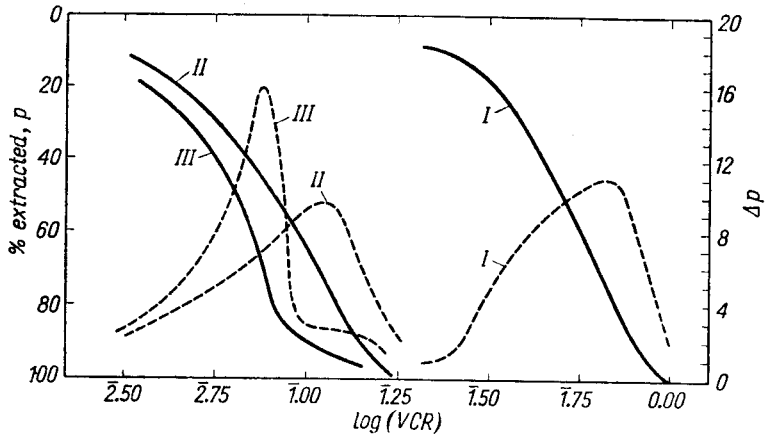


FIG. 107. Viscosity–concentration ratio ($\log_{10}$ VCR) (plain lines) and distribution of $\log_{10}$ VCR of fractions of nitrocotton (broken lines), according to G. G. Jones and Miles [16a]. Designation of samples as in Fig. 106.

to express the viscosity in terms of viscosity–concentration ratio (VCR) which is the specific viscosity, and the quantity of the component extracted, of different nitrogen content.

Extensive research into the fractional partition of nitrocellulose by means of acetone–water mixtures was carried out by Rogovin and Glasman [111]. The results of these experiments are given in the Table 59.

TABLE 59

VISCOSITY OF FRACTIONS OF NITROCELLULOSE

Nitrocellulose fractions	Viscosity of a 2% solution in acetone sec
I	16–17
II	33–34
III	54–62
IV	62–115
V	420
VI	690–1000

The method of fractionating by dissolution has also been used to determine the length of cellulose chains: nitration by means of nitric acid mixed with phosphoric acid does not bring about any degradation of practical importance. The molecular chains of nitrocellulose produced in this manner are as long as those of the original cellulose, hence different fractions do not differ with regard to their viscosity. Schieber [112] used a mixture of alcohol and ethyl acetate in which proportion of the acetate was augmented step by step.

Krüger [113] tried fractionating nitrocellulose by diffusion. The principle of the method was that a nitrocellulose solution in acetone, methyl alcohol or amyl acetate diffused into a pure solvent layer on the surface of the solution. Clearly molecules of smaller size penetrate more rapidly. A nitrocellulose solution of 12.8% N was separated into two layers in this way after 42 days' diffusion. The lower fraction comprised nitrocotton with a nitrogen content of 13.1% N, the upper layer one of 12.1% N.

Fractionating nitrocellulose by means of ultra-filtration was carried out by Duclaux and Wollmann [101]. Using filters differing in pore sizes, nitrocellulose of 11.0–12.5% N was separated into fractions of different viscosity ranging from 0.08 to 3.7. The molecular weight of the fractions, determined by the osmotic pressure method, was found to range from 21,000 to 70,000. Differences in the nitrogen content of the fractions was negligeable.

The distribution of molecular weights in nitrocellulose solutions has been studied by other methods, e.g. Svedberg's ultra-centrifuge method (Svedberg and Gralen [114] and Jullander [115]). Svedberg and Gralen have also made use of this method to determine the molecular weights of cellulose and nitrocellulose, and hence the degradation of the cellulose chain during nitrating. The results of these experiments are reported elsewhere (see. p. 343).

The fractionating of nitrocellulose by chromatographic absorption has also been described. As reported by Claesson [116] a 1.5% nitrocellulose solution in

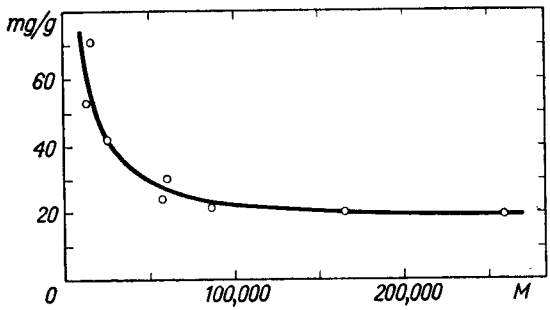


FIG. 108. Chromatographic separation of nitrocellulose fractions (quantity of fractions in mg/g and their molecular weight M; Claesson [116]).

acetone was absorbed on activated charcoal in differing amounts that correspond with the molecular weight. This relationship is illustrated by the diagram (Fig. 108). The higher the molecular weight, the less it is absorbed by the charcoal. Nitrocellulose can be also fractionated on starch.

There is no doubt that even the most uniform nitrocellulose, the nitro group content of which corresponds to trinitrate, is not a chemical individual in the usual sense of the term. The substance is composed of chains of different length, hence it is non-homogeneous.

HYGROSCOPICITY

As early as 1894 it was found that the lower the nitrogen content of nitrocellulose, the larger the amount of moisture it absorbs. Extensive research on the hygroscopicity of nitrocellulose was carried out by Will [117]. At an atmospheric humidity exceeding 90%, but below that at which condensation of vapour occurs on the nitrocotton owing to fluctuation of temperature, there exists a distinctive relationship between the nitrogen content of nitrocellulose and the amount of moisture absorbed. The more nitrate groups there are present in the molecule the fewer the available hydroxyl groups, and the less hygroscopic the nitrocellulose. This is due to the fact that molecules of water associate by means of hydrogen bonds with free, non-esterified HO-groups in the nitrocellulose.

It has been reported by Will that for nitrocelluloses with nitrogen content from 9.0 to 13.3%, dried to a constant weight at the temperature of 40°C, the percentage sum of the nitrogen content and of the absorbed mixture was constant equal, on average, to 14.6:

$$\%N + \%H_2O = 14.6$$

This simple formula has not been fully confirmed in later investigations, however. Thus Demougin [118] from his own investigations on the hygroscopicity of nitrocellulose containing from 10.94 to 14.1% of nitrogen has come to the conclusion that Will's rule could only be valid in atmospheres of low humidity. As the moisture content of the atmosphere approaches saturation point, the physical shape of the nitrocellulose, and hence the state of its surface, and the diameter and number of capillaries varied. De Pauw [119] then found that for nitrocelluloses containing 12.3 to 13.8% N the sum of the nitrogen content and of the hygroscopic moisture content was not constant, but was higher the lower the nitrogen content of the nitrocellulose. So for nitrocellulose with a 12.3% N the sum amounts to 17.1, whereas for 13.8% N it is 16.4.

In spite of the variability of the sum calculated from the nitrogen content and hygroscopicity the effect of the nitrogen content on the hygroscopicity can be expressed by a straight line. In Fig. 109 (after de Pauw) straight-lines corresponding with different relative moistness of atmosphere (f/F) are shown.

Water absorption from a 40% calcium nitrate solution was studied by Gukhman, Petrov and Yakovlev [120], who found that a nitrocellulose film immersed in such a solution was capable of absorbing up to 50% of water. After 5 min the water content reached 15–20%, and after 15 min it amounted to 25–30%.

From the practical point of view the absorption of acids by nitrocellulose is of major importance for the question of stabilizing nitrocellulose. It has been established (Wiggam [121]) that nitrocellulose absorbs dilute nitric acid and dilute sulphuric acid to the same extent, the absorption of hydrochloric acid being somewhat less.

The capacity of nitrocellulose to absorb vapours of organic solvents from the

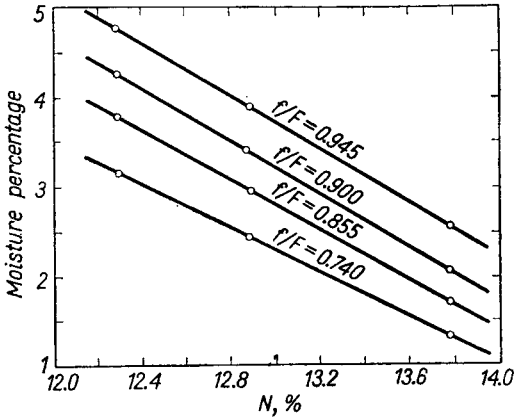


FIG. 109. Hygroscopicity of nitrocellulose as a function of nitrogen content (de Pauw [119]).

air has also been investigated. Here again the amount of substance absorbed depends on the nitrogen content of the nitrocellulose. According to Jenkins, Bennet and Rubenstein [122, 43]) there exists a certain maximum nitrogen content, characterized by the highest absorption capacity of nitrocellulose. Nitrogen values greater or less than this lower the absorption capacity. In the case of acetone, maximum absorption is attained at 12% N.

The absorption of vapours is accompanied by a positive thermal effect. Kargin and Papkov [123] measured the heat developed when acetone or pyridine were absorbed by nitrocellulose from petroleum ether or from a pure solvent, and found it was about 20 cal/g for acetone, and about 30 cal/g for pyridine.

The heat of absorption of acetone, ethanol, or ether by nitrocellulose was reported by Calvet [124]:

nitroramie 14% N:	ethanol	1.30 kcal/mole solvent
	ether	2.50 kcal/mole solvent
	acetone	3.88 kcal/mole solvent
nitroramie 11.5% N:	ethanol	1.80 kcal/mole solvent
	ether	3.37 kcal/mole solvent
	acetone	4.09 kcal/mole solvent

The heat of absorption of a mixed solvent: ethanol + ether, has been determined by the same author. The value varied according to the composition of the solvent reaching its maximum value at an ether: ethanol mole ratio of 1:1.3. The same solvent gave the maximum absorption heat both with high-nitrated and low-nitrated nitrocellulose. The thermal effect was appreciably larger for lower nitrated nitrocellulose. This seems to confirm Highfield's theory (see pp. 248, 256) that molecules of alcohol form bonds with the free hydroxyl groups of nitrocotton, thus producing a complex compound soluble in ether.

Other sources (Calvet and Izac [125]) report a value of 67.5 cal/g for the heat of absorption of acetone.

The investigations of Kargin and Stepanova [126] indicate that the heat of solution of nitrocellulose is slightly greater than the heat of absorption. The heat of solution was discussed on pp. 248–249.

OPTICAL PROPERTIES OF NITROCELLULOSE

Like cellulose, nitrocellulose demonstrates optical anisotropy (double refraction) which is regarded as one of the facts confirming the microcrystalline structure of the substance. A relationship between this property of nitrocellulose and the nitrogen content has been discovered by Ambronn [127] who studied the double refraction of cellulose. Differences in the refractive index for rays of different wave-lengths in two directions at right angle are of the order -0.50×10^{-3} to $+2.8\times10^{-3}$ (Table 60).

TABLE 60

DIFFERENCES OF REFRACTIVE INDICES ALONG TWO PERPENDICULAR DIRECTIONS FOR DIFFERENT WAVE-LENGTH

Nitrocellulose with nitrogen content, %	435 mμ	546 mμ	579 mμ	650 mμ
13.16	−0.50	−0.32	−0.31	−0.23
12.85	−0.32	−0.20	−0.17	−0.12
11.88	−0.12	−0.08	0	+0.02
10.55	+0.35	+0.32	+0.31	+0.30
cellulose	+2.8	+2.2	+2.07	+1.91

The data show that nitrocellulose containing 11.88% of nitrogen is isotropic for a wave-length of 579 mμ. Isotropic properties have also been established with nitrocellulose in a colloidal state, the phenomenon being attributed to the unoriented state of the micelles. However stretching a solid colloidal mass of nitrocellulose (celluloid) mechanically is sufficient to produce the anisotropic effect, since elongation of the micelles (and molecular chains bound by covalent bonds) causes them to orient and align themselves in the direction of the stretching force (Wächtler [128]).

These investigations agree well with experiments by Trillat [129] who found that the X-ray diagram of colloidal nitrocellulose showing a non-oriented structure of crystallites (interference rings), altered after being stretched to indicate a fibrous structure in which the crystallites were oriented along the axis in the direction in which the film was stretched.

Under the polarizing microscope nitrocellulose acquires different colours. According to Tissot [130] the different colours of nitrocellulose (11.6–12.55% N) seen through crossed nicols depended on the nitrogen content of nitrocellulose, but his conclusions were subjected to strong criticism in the later work of Phillips [131], who found that the colour of nitrocotton in polarized light does not depend on the nitrogen percentage, but it is related to the degree of aggregation of the nitro-

cellulose molecules. A red colour is seen when the degree of dispersion is high and blue when it is low.

Nitrocellulose fibres of different nitrogen content, suspended in glycerine, were investigated in a polarizing microscope by Miles [132]. He classified the samples into three groups:

(1) steel-grey to bluish-grey: below 11.0% N
(2) yellow to brownish-yellow: 11.4 –11.8% N
(3) blue: over 11.8% N

More recently the experiments with polarized light have been extended to gelatinized nitrocellulose.

A solvent containing 80% of nitroglycerine and 20% of nitroglycol to which 0.02% of crystal violet had been added was used by Fenson and Fordham [133]. The technique of adding a dyestuff to a solvent when investigating the process of dissolution of nitrocellulose was first described in a paper by Mangenot and Raison [134]. Using Sudan Red or Indophenol Blue, they succeeded in following the gradual progress of solution from the initial swelling of the nitrocellulose until the fibre ceased to be visible. The transformations taking place in the interior of fibres could be seen by following the absorption of the dyestuff.

Fenson and Fordham report observing in polarized light the colours listed in Table 61.

TABLE 61

THE COLOUR OF NITROCELLULOSE IN POLARIZED LIGHT

Nitrogen content of nitrocellulose %	Colour
11.4	pale red to grey
11.5–11.8	pale yellow, brown to red
11.9	neutral
12.0–12.6	pale blue to grey
12.6	light blue to greenish white

Both Mangenot and Raison, Fenson and Fordham have established from their microscopic studies on swelling and solution of nitrocellulose fibres that the surface of the fibres consists of a thin coating of a distinctively less soluble substance than the interior of fibres. Fenson and Fordham assumed that this was a superficial layer that had been partially denitrated in consequence of drastic stabilization processes. Therefore in the instance of a nitrocellulose of 11% N a solvent penetrates into the fibres through the damaged points of this layer.

Unpublished microscopic experiments of T. Urbański [29] on the dissolution of nitrocellulose fibres provide additional evidence that there exists a layer hindering the action of solvents, since the fibre starts to dissolve at the ends which have been torn and frayed by passage through the beaters.

The absorption spectrum of nitrocellulose solutions has been examined (Rassow and Aehnelt [135]). It has been established that the capacity to absorb light differs with the origin of the nitrated cellulose. Thus nitrocellulose made from wood pulp gives a slightly different absorption spectrum from that of nitrocotton.

G. G. Jones and Miles [136] examined the ultra-violet absorption spectra of nitrocelluloses having a range of nitrogen contents from 10.9 to 14.1%. The absorption curve shows a maximum close to 220 mμ, and an inflection below 300 mμ. The extinction is relatively small ($\varepsilon = 15.0$). This is typical of aliphatic compounds which lack a conjugated double bond system and give only the "R" spectrum.

Experiments by Ellis and Bath [137] on the infra-red absorption spectrum of cellulose have indicated the existence of hydrogen bonds between the hydroxyl groups of the cellulose molecules, probably following the —O—H···O— pattern (see p. 225).

An extensive analysis of infra-red absorption spectra has been carried out by

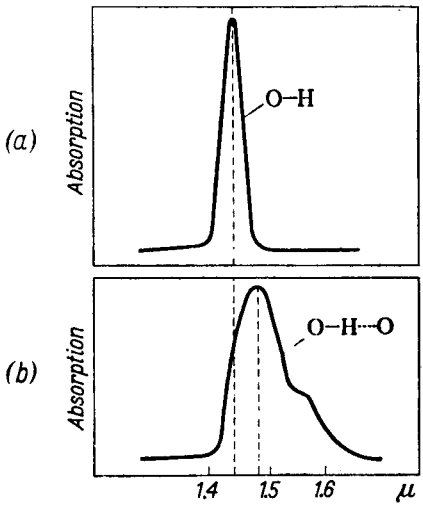


FIG. 110. Hydroxyl bands in infra-red spectrum of cellulose (Nikitin [138]).

Nikitin [138] who investigated native cellulose, mercerized cotton, cellulose esters (nitrates, acetates), and cellulose ethyl ether. Cellulose gave a number of the overtone absorption bands between 6711 and 4739 cm^{-1} that correspond to the overtone vibrations of hydroxyl groups bound by hydrogen linkages. These bands disappear as the hydrogen atoms of the hydroxyl radicals are substituted. In the spectrum of a cellulose dinitrate of 12.8% N, the band 3571 cm^{-1} appears caused by the hydroxyl groups freed from hydrogen bonds. A "trinitrate" containing 13.7% of nitrogen does not give any of those bands. Instead another band of 1639 cm^{-1} occurs, belonging to the O-nitro group. Well in line with these data are the results of Barchewitz, Henry and Chédin [139]. Two maxima in the infra-red absorption spectrum, charac-

terizing the O-nitro group, i.e. about 1667 and 1282 cm^{-1} have been found by Champetier and Clément [140]. Similar results have been reported by Zhbankov [141].

Nikitin has proved that in cellulose obtained by regeneration of nitrocellulose, the bands typical for hydrogen bonded OH group reappear. The curve in Fig. 110a represents the absorption band of cellulose dinitrate due to the presence of a OH group. After the regeneration of cellulose the absorption curve on Fig. 110b is obtained with the band shifted and widened owing to the hydrogen linkage.

ELECTRICAL PROPERTIES OF NITROCELLULOSE

It has been demonstrated experimentally on an industrial scale that nitrocellulose is readily charged with static electricity by friction, even by the air current during drying. Dry nitrocellulose charged with electricity may ignite on discharging.

Lee and Sakurada [142] have examined the dielectric constant of nitrocellulose dissolved in acetone and in acetone–hexanone mixtures. They found that the dielectric constant was only very slightly dependent on the viscosity, and completely independent of the concentration.

Among other electrical properties of nitrocellulose, attention should be paid to the experimental work on the electrical conductivity of solutions. Thus Dobry [143] found the conductivity of a nitrocellulose solution in acetone to be proportional to its concentration. Experiments on the electrophoresis of solutions made by Lantz and Pickett [144] demonstrated that the particles of nitrocellulose carry a negative charge. Electrolysis of the solution causes the nitrocellulose gel to collect at the anode. This gel may contain the metal of which the anode is constructed, as demonstrated by Apard [145].

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CHAPTER XI

CHEMICAL PROPERTIES OF NITROCELLULOSE

STABILITY

ONE of the most important problems in nitrocellulose technology concerns the purification process intended to increase as far as possible the stability of the product.

In the initial period of nitrocellulose manufacture numerous catastrophic explosions took place due to insufficient purification of the product. The purification method developed by Lenk [1] was then in use:

(1) washing nitrocellulose for at least two weeks with running water;

(2) boiling for several minutes in a 2% sodium carbonate solution and keeping in concentrated sodium silicate solution;

(3) rinsing with water and drying.

It became clear, however, that the methods introduced by Lenk were not sufficient to ensure a high enough chemical stability of the product. Also it became clear that a systematic study of stability and stabilization of nitrocellulose are needed.

The first study of the stability of nitrocellulose seems to be that of de Luca [2]. It is described below (p. 307).

A turning point in the field of stabilizing nitrocellulose was reached when Abel [3] discovered in 1865 that a certain amount of acid is retained within the channels extending along the fibres and this was causing the lack of stability of the nitrocellulose then produced. According to Abel stable nitrocellulose can be obtained by longer boiling of nitrocotton fibres cut in short pieces.

Later it was proved experimentally that the resistance of nitrocellulose to heating was dependent on the composition of the mixed acid, thus on the quantitative proportions of its three ingredients: sulphuric acid, nitric acid and water. With a high concentration of sulphuric acid in the nitrating mixture the nitrocellulose stability is reduced as established by Lunge's work mentioned below. Simultaneously it was suggested (Cross, Bevan and Jenks [4], Berl and Klaye [5]) that during nitration initially sulphuric acid esters are formed which are afterwards interchanged with nitric acid. The result is that cellulose nitrates or mixed sulphuric and nitric acid esters are produced, the latter if the chemical exchange is incomplete. These

researches suggested that the mediocre stability of nitrocellulose might be due to the sulphuric acid esters or mixed cellulose sulphate–nitrates present in the product (Hake and Lewis [6]).

In point of fact it has been established by many workers that a nitrocotton freshly produced and washed from acid could contain up to 8% of sulphuric acid cellulose esters. Berl and Boltenstern [7] stated in later investigations that sulphuric acid always occurred in the stabilized nitrocotton in two forms: (a) as an inorganic salt, for the most part $CaSO_4$; (b) as sulpho groups chemically combined with cellulose. Their data are given in Table 62.

TABLE 62

SULPHURIC ACID CONTENT IN STABILIZED NITROCELLULOSE

Nitrogen content in nitrocellulose, %	Sulphuric acid content, %		The ratio of the total amount of acid to the part bonded as inorganic salts
	total amount	bonded as inorganic salts	
11.20	0.24	0.12	2:1
11.88	0.16	0.12	1.3:1
12.45	0.16	0.10	1.7:1
13.00	0.27	0.12	2.3:1
13.19	0.25	0.10	2.4:1
13.25	0.27	0.13	2.1:1

According to Hess, Trogus and Tomonari [8] mixed sulphuric and nitric esters of cellulose are soluble in methyl alcohol. Hence by boiling nitrocellulose in methyl alcohol it is possible to remove these substances up to a quantity corresponding to some 1% of the nitrocellulose mass. The extracted product contains three NO_2 and two SO_3H groups for every two $C_6H_{10}O_5$ units.

An appreciable advance towards explaining the essential basis of stabilizing nitrocellulose, and towards inventing an adequate stabilization process came from the studies of R. Robertson [9]. He has stated that the sulpho groups in cellulose sulphates and sulphate–nitrates undergo a quick and complete decomposition when boiled in the presence of dilute acids. Alkaline boiling on the other hand, causes the mixed ester to decompose very slowly and incompletely. This is why in practice prolonged boiling of at least 20 up to 100 hr in pure water is recommended as the first operation. The water becomes quickly acid during boiling due to the presence of acid absorbed or formed from the decomposition of unstable esters. According to Robertson this hydrolysis is most effective, when about 1% of sulphuric acid is present in the water. After changing the water and repeating the boiling in fresh water, a mild alkaline boiling (most preferably using calcium carbonate) can be carried out in order to neutralize the acid products formed during the previous treatment. If the alkali is added too soon to the water it may check the process of stabilization, since any incompletely hydrolysed sulphuric acid esters present are capable of

forming salts in the alkaline stabilizing liquor, for instance calcium salts, difficult to dissolve in water, and to decompose.

Goujon [10] also found it necessary to begin the stabilization with an "acid boiling", and he confirmed the danger of too early an alkalization of the stabilizing bath. It has been found (Demougin and Landon [11]) that the stabilizing capacity of acids decreases in the following order: HNO_3, HCl, H_2SO_4.

Later experiments were carried out with a nitrocellulose stabilization process that consisted in treating a partially purified nitrocotton in an ammonia bath (e.g. Reeves and Giddens [12]). This was based on the supposition that ammonia was capable of neutralizing accurately acids contained in the interior of nitrocellulose fibres. However, this method has not been adopted in practice, since it was feared that the sulpho groups attached to cellulose in the form of mixed esters would undergo only partial hydrolysis in the presence of ammonia and later spontaneous hydrolysis of these substituents in the finished (stabilized) product might reduce its stability.

On the basis of his extensive works on the sulpho groups attached to cellulose in the form of neutral esters $R_{cel}OSO_2OR_{cel}$ and hydrogen sulphates $R_{cel}OSO_2OH$, Kullgren [13] concluded that stabilization should be begun immediately after the spent acids are removed from nitrocellulose.

Cellulose nitrated with nitric acid vapour or by means of $HNO_3+N_2O_5$ mixtures demonstrates a significantly higher stability than nitrocellulose nitrated in a mixture of nitric and sulphuric acid. This provides further evidence that the presence of sulphuric esters in nitrocellulose is responsible for its low stability.

Very extensive investigation made by A. C. Smith [14] showed that nitrocellulose with a low nitrogen percentage contained cellulose hydrogen sulphate, whereas in nitrocellulose with a high nitrogen content, sulphuric acid and oxidation products of cellulose were detected. For this reason, nitrocellulose with a relatively low degree of nitration approaching 12% N or slightly exceeding 12% is particularly easily stabilized.

Smith carried out his experiments by means of the following technique: nitrocotton removed from the nitrating acid was washed in running water until the water was no longer acid. The total acid content (by titrating its acetone solution), and the concentration of sulphuric acid esters were determined in the products. The results are shown in Table 63.

An interesting observation has been made while attempting to purify nitrocotton by dissolving it in acetone followed by precipitation with water. Guncotton (sample 1) was fairly well purified and stabilized by this method, but collodion cotton (sample 4) retained almost the whole amount of acid present in it before purification and it was just as unstable as before, because the sulphuric esters were dissolved and reprecipitated with the nitrocellulose. Incidentally this is convincing chemical evidence confirming the existence of sulphuric acid cellulose esters in lower nitrated cellulose.

Smith also stated that the sulphuric acid content in nitrocotton was dependent of the proportion of H_2SO_4 in the mixed acid. Thus if the sulphuric acid content

TABLE 63

SULPHURIC ACID AND ITS ESTERS IN NITROCELLULOSE (SMITH [14])

No.	Type of nitrocellulose	Nitrogen content %	H_2SO_4 as free acid %	H_2SO_4 as nitrocellulose hydrogen sulphate %
1	Guncotton	13.4	0.69	0.08
2	Pyrocollodion cotton	12.6	0.44	0.16
3	High-viscosity collodion cotton	12.1	0.17	0.30
4	Low-viscosity collodion cotton	10.7	0.00	0.52

of the nitrating mixtures was increased from 18 up to 64%, the product of 13.4% N included from 0.16 to 0.68% of sulphuric acid.

Similar observations were also published earlier by Tribot and Marsaudon [16]. Recently, however, Lhoste [17] has questioned the validity of the hypothesis of the formation of sulphuric acid esters during the nitration of cellulose. On the basis of analytical data the author has arrived at the idea that sulphuric acid is bound with nitrocellulose solely by occlusion. He found no evidence to confirm the existence of cellulose sulphates in nitrocotton.

The values reported by Lhoste comparing the total amount of sulphuric acid with the amount of sulphuric acid bound in nitrocellulose before stabilization, and then at the time of stabilization boiling in distilled water, are collected in Table 64.

TABLE 64

CONTENT OF SULPHURIC ACID IN NITROCELLULOSE (IN % OF THE H_2SO_4) (AFTER LHOSTE [17])

Nitrogen content %	Sulphuric acid	Stabilization boiling, hr						
		0	5	10	25	50	100	200
13.40	Total	0.753	0.332	0.270	0.143	0.110	0.054	0.020
	Free	0.760	0.279	0.251	0.120	0.080	0.077	0.039
12.52	Total	0.517	0.047	0.040				
	Free	0.481	0.056	0.034				
11.24	Total	0.401	0.019					
	Free	0.385	0.028					

The analytical results for total and free sulphuric acid figures do not differ within the limits of experimental error.

It follows from these figures that practically all the sulphuric acid is bonded.

Lhoste has also drawn attention to the fact that the rate of removal of sulphuric acid from nitrocellulose depends on its nitrogen content. The more highly nitrated the nitrocotton, the more slowly sulphuric acid is eliminated from it. Thus in the instance of nitrocellulose of 13.40% N, a 100 hours' boiling is necessary to attain the same sulphuric acid content as that of nitrocellulose with 12.19% N-content boiled for 10 hr.

Lhoste's views are rather unexpected for they are contrary to those of most of the other authors and particularly of A. C. Smith (p. 295).

Certain differences in numerical data reported in various publications can be justified to some extent by differences in the analytical methods used. On the other hand, the values given by Lhoste seem to show that the sulphuric acid in nitrocotton could be combined with nitrocellulose molecules less firmly than in an ester group. For instance, it is not out of the question that sulphuric acid may be bound with nitrocellulose as an inclusion (clathrate) compound. (Attention was also drawn to this point by Miles [15] in his monograph on cellulose nitrate.)

The content of sulphuric acid may also depend on the type of cellulose nitrated, according to Gagnon, Keirstead and Newbold [18].

Research into the course of partial nitrocellulose denitration occurring during stabilization boiling has provided material for a further inquiry into the question of removing both sulphuric acid, and sulpho groups contained in nitrocotton during the stabilization process.

This problem was first investigated by Vieille [19]. Later Chédin and Tribot [20] made a detailed study of the composition of the acids that passed into the water while nitrocellulose was boiled for long periods. Nitrocotton of 13.2% N was prepared by means of the usual mixed acid containing 22% of nitric acid. The results of the experiments are illustrated in Fig. 111. Up to 90 hr the concentration of both of acids in water increased rapidly. Thereafter it slowed down. The increase of nitric acid concentration in the water became less marked while the amount of sulphuric acid no longer increased. The ordinates between *I* and reference line *III* indicate the evolution of nitric acid which is constant (*ca.* 2.48) at any time of the second stage of the hydrolysis. The loss of nitric acid during 90 hr was 2.80% corresponding to a 0.62% nitrogen loss by the nitrocellulose. Such a strongly marked denitration demonstrates the difficulties of manufacturing high-nitrated nitrocellulose by the usual methods, even if the product obtained immediately after the nitration has a nitrogen content approaching that of cellulose trinitrate [15].

In order to explain the limited stability of not fully purified nitrocotton a theory has been developed that at the time of esterifying cellulose hypothetic nitrous acid esters are formed alongside nitric esters under the influence of nitrogen dioxide, present in the nitrating acid. This suggestion was apparently confirmed by Nicolardot and Chertier [21] who assumed they had prepared cellulose nitrites as they treated a suspension of cellulose in dilute nitric acid by means of nitrous acid. Cellulose nitrites were separated from the nitrates by dissolving the latter in acetone. These cellulose nitrites were described by the authors as a grey, hygroscopic powder, containing about 2.5% of nitrogen, immiscible with water and organic

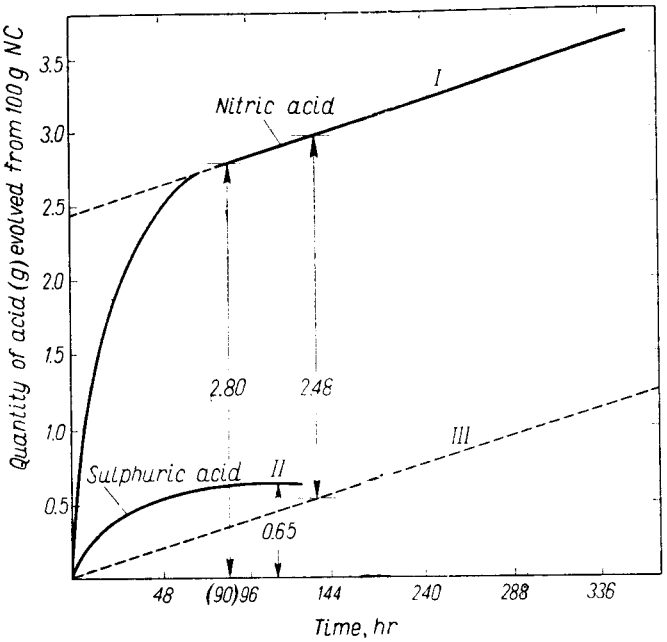


FIG. 111. Production of acids by boiling guncotton (13.2% N), according to Chédin and Tribot [20] and Miles [15].

solvents. There is some doubt however, whether the substance was not composed of cellulose oxidation and nitration products.

Furthermore, certain nitrocellulose degradation products, for example organic acids, exert an adverse influence on the stability of nitrocellulose. That the stability of nitrocellulose is raised by washing it with an alcohol can be quoted in support of this view. Thus as a quick laboratory stabilization method boiling nitrocotton with methyl alcohol (Tomonari [22]) or with ethyl alcohol (Muraour [23]) is recommended. In accordance with the investigations of Hess, Trogus and Tomonari [8] already cited, methyl alcohol is capable of removing not only the degradation products, but also mixed esters of sulphuric and nitric acids.

Following the changes in the properties of nitrocellulose during stabilization boiling, Will [24] has come to the conclusion that the higher the nitrogen content, the longer stabilization boiling is necessary. Thus for every nitration degree the substance should be boiled for a certain, determined interval of time in hours. According to Will a well stabilized nitrocotton can be recognized by the fact that on heating at 134.5°C in a stream of carbon dioxide, it breaks down to produce nitrogen at a steady rate:

$$\frac{\Delta n}{\Delta t} = \text{const.}$$

where Δn = the amount of nitrogen lost by the nitrocellulose at time Δt.

Insufficiently purified, non-stabilized nitrocotton demonstrates a variable value of $\Delta n/\Delta t$. The evolution of nitrogen as a function of time is illustrated in the diagram (Fig. 112). The curves *I–IV* relate to nitrocellulose of a high nitrogen content (13% N) boiled in water for different periods from 30 to 100 hr. The longer the time of boiling, the more the curve approaches a straight-line. Finally, after 100 hr

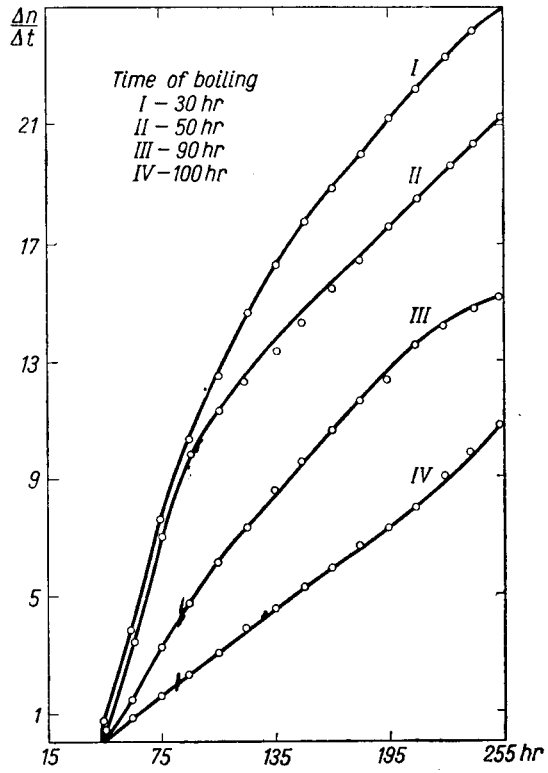


FIG. 112. Decomposition of nitrocellulose of different stability at 134.5°C, according to Will [24].

a straight line is attained. Will therefore assumed that in order to stabilize such nitrocellulose at least 100 hr boiling is needed.

On the basis of his results already quoted, Goujon [10] also concluded that there exists a threshold stability of nitrocotton that can be achieved by sufficiently prolonged stabilization boiling. Using the Taliani test Goujon determined the pressure of the gases evolved on keeping nitrocellulose at the temperature of 135°C. He found the time necessary to attain the threshold stability to be nearly twice as long as that indicated by Will. Thus in the instance of guncotton No. 1, i.e. nitrocellulose of 13.3% N, Will considers 120-hours' boiling is indispensible, whereas Goujon recommends 240 hr. In the case of guncotton No. 2. with a nitrogen content of 12.0%, Goujon considers 24-hours' boiling followed by washing with water containing calcium carbonate, to be long enough.

When the threshold stability has been attained, further boiling does not improve the nitrocellulose any more and the gradient $\Delta n/\Delta t$ at any temperature is dependent on the nitrogen value of the nitrocellulose (Fig. 113).

The stabilization time may be considerably shortened if the product is boiled in water under pressure. Data from Goujon's paper reported below show to what extent the time of boiling was shortened by using autoclaves for the stabilization

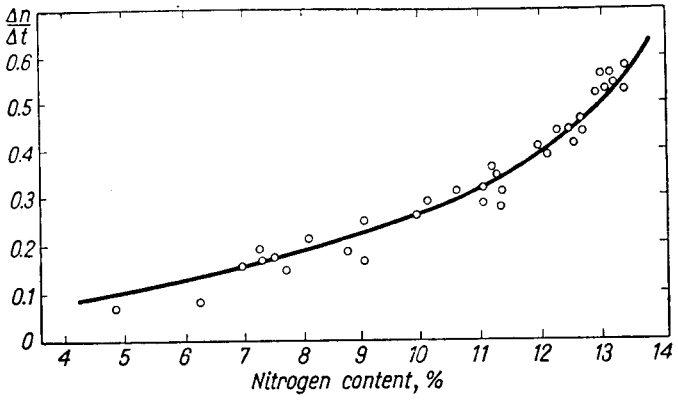


FIG. 113. Rate of decomposition of nitrocellulose (Δ_n/Δ_t) as a function of nitrogen content (Will [24]).

of high-nitrated cotton (CP_1, p. 373). Boiling at 100°C for 120 hr is equivalent to a boiling:

at 110°C for 30 hr
at 120°C for 16 hr
at 130°C for 6 hr

In practice the following principle of stabilization boiling is generally accepted. First prolonged boiling is carried out without changing the water. The water becomes more and more acid due to the acid substances released by the product. This fundamental stabilizing operation should be prolonged as long as possible. According to Goujon, for guncotton No. 2 (CP_2) it should last 15–20 hr, for guncotton No. 1 (CP_1) 72–96 hr, whereas for very high-nitrated guncotton 120–192 hr are necessary. The water is then filtered off, the nitrocotton may be rinsed, and then boiled again for a short time. Finally the fibres are pulped and given an alkaline boiling or washing in the presence of calcium carbonate.

In more up to date processes nitrocellulose a boiling under atmospheric pressure is first given and then heated for a short time in an autoclave, under pressure, at a temperature of 140°C. This results in an appreciable saving in the total time required for stabilization. Stabilization by acting with readily absorbed substances [97] and in solvents (p. 392) was also reported.

Hess *et al.* [25, 8] carried out X-ray investigations of nitrocellulose during the stabilization process. In the X-ray diagrams of the nitrocotton fibres immediately after nitration, almost no interference rings were visible. They appear

only after acid is removed by thorough washing. As the result of prolonged stabilization in 50% acetic acid, or of boiling the substance in methyl or ethyl alcohol, sharp diagrams are obtained (Fig. 87, p. 241).

Since on stabilization the outlines of interference rings became more distinctive, new rings became visible, while simultaneously ones formerly perceptible disappeared, the authors suggested that owing to chemical processes during stabilization, nitrocellulose undergoes a certain transformation in crystalline structure. Further the changes in the X-ray diagrams also depend on the composition of the mixed acid. Thus if mixed acid poor in water is used to yield a product with a nitrogen content of about 14%, a substance giving the X-ray diagram characteristic of cellulose trinitrate is formed immediately on nitration with a mixture containing a large proportion of nitric acid. When nitration is carried out with an HNO_3 concentration between 18 and 46%, the change in the X-ray diagram mentioned above takes place during stabilization of the product.

Ropuszyński [26] recently reported that the action of a magnetic field during the boiling of nitrocellulose in water produces a beneficial effect on the stability of nitrocellulose.

For example, nitrocellulose of 13.0% N made from wood cellulose, boiled for 74 hr, was compared with a product subjected to the same treatment in conjunction with the action of a strong magnetic field.

The results of pH measurement of samples heated at 120°C were:

	pH after 2 hr	after 4 hr
nitrocellulose boiled, initial pH = 6.95	3.36	2.78
nitrocellulose subjected to the action of magnetic field and boiled, initial pH = 6.95	4.61	3.21

In spite of the most extensive investigations into the stabilization of nitrocotton, the essence of the process has not yet been made clear. It seems that the removal of unstable products present in the nitrocotton alone cannot explain sufficiently clearly the stabilization of nitrocellulose by stabilization boiling. It has also been suggested that cellulose nitrate directly after nitration has an unstable chemical structure, e.g. a peroxy structure. It was assumed that this structure proceeds to a stable system during boiling. As indicated by the X-ray investigations of nitrocotton at different stabilization stages, mentioned above, at the time of the stabilizing boil a change in the microcrystalline structure of the compound takes place. This structural change may well exert an influence upon the stability of the nitrocellulose.

COMPLEX COMPOUNDS

Apard [27] found that the addition of finely powdered plumbous oxide, calcium oxide or calcium hydroxide to a 1% nitrocellulose solution in acetone, ether–alcohol or amyl acetate initially brought about an increase of the viscosity. Further addition of these substances caused the nitrocellulose to coagulate, together with the added

metals. Apard therefore considered that nitrocotton formed complex compounds with these oxides.

Rogovin and Shlakhover [28] report that nitrocellulose produces a complex compound with calcium hydroxide. If coagulation does not take place, then an increase in viscosity is observed in the presence of calcium hydroxide (Glikman [29]).

It has likewise been shown by Morozov [30] that it is possible to coagulate nitrocellulose under the influence of boric acid, in the presence of the following metal oxides: Mn, Fe, Ni, Cu, and Zn. This author noticed that the nitrocotton gel formed owing to the influence of the oxides redissolved in the course of time, probably as a result of a change in chemical composition. On the other hand, the precipitate obtained by treating nitrocellulose with plumbous oxide or aluminium oxide is insoluble. Papkov and Khveleva [31] have established that a similar coagulation takes place under the influence of such salts as: zinc sulphate, magnesium chloride and aluminium chloride.

It has long been known that nitrocotton may be precipitated from solution in the form of a gel on the addition of a metallic powder, e.g. copper, aluminium. Jenkins [32] examined the activity of different metals as coagulating agents, and found lead to be the strongest, and zinc the weakest coagulating agent. The metallic powders studied have been ranged with respect to this property to form a series as follows:

$$Pb > Ca > Ag > Sn > Fe > Cu > Zn$$

The addition of different organic acids weakens the effect or prevents it altogether. The strongest anticoagulating activity is that of maleic acid.

Gloor and Spurlin [33] are of the opinion that compounds are formed between the nitrocellulose and the powdered metal by means of the secondary valencies. They have demonstrated that the higher the molecular weight of the nitrocotton, the smaller the quantity of metal powder necessary to cause the gel to coagulate.

It was further observed by Pamfilov, Shikher and Shikher [34] that the less the nitrocellulose had been stabilized the quicker the precipitation of gel. On this basis it was assumed that traces of acids accelerate the coagulation process. According to Vodiakov [35] the quantity of metal or metal oxide combined or absorbed in the gelatinized nitrocellulose is approximately proportional to its nitrogen content.

A hypothesis has been published by de Waele [36] that nitrocotton combines with metallic oxides (pigments) through the carboxylic groups. The latter are present in partially oxidized derivatives of cellulose that accompany nitrocellulose. More recently Campbell and Johnson [37] have come to conclusions similar to those of Vodiakov and of de Waele.

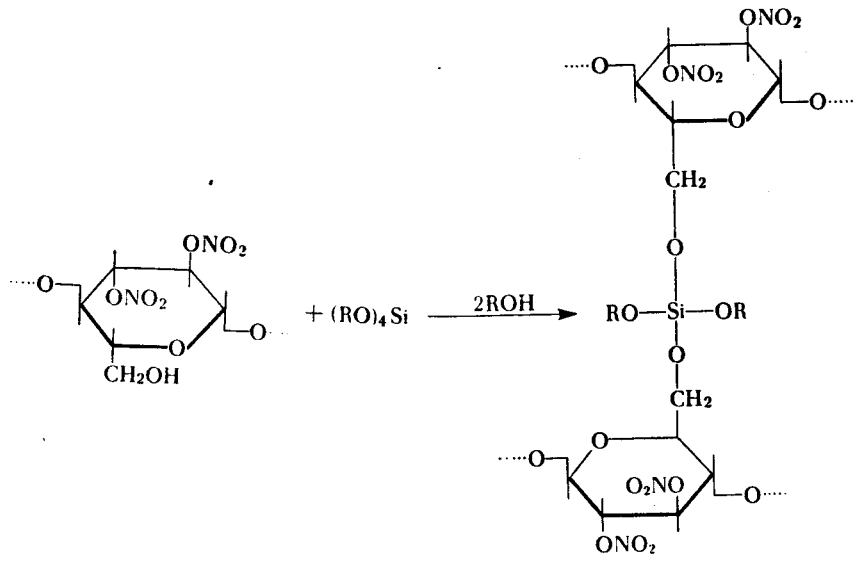
Taking into consideration the nature of the complex compounds between nitrocotton and metals or metal oxides, Miles [15] suggested that they approach in chemical character the cuprammonium complexes of cellulose.

CROSS-LINKING
(INCREASING THE VISCOSITY BY MEANS OF CROSS-LINKING)

There exist instances where an increase in the viscosity of nitrocellulose solutions is recommended as in the product intended for manufacture of blasting gelatine, i.e. for the solution of nitrocellulose nitroglycerine. The solution must have the consistency of firm gelatine.

Jullander [38] has proposed reacting nitrocellulose 12.2% of N with inorganic acid polychlorides such as $SiCl_4$, PCl_5, $POCl_3$, or with chlorides of dicarboxylic acids, e.g. oxalyl chloride. T. Urbański and G. K. Jones [39] used thionyl chloride for the same purpose and Bouchez [94] sebacyl chloride. There is no doubt that these substances react with free hydroxylic groups to form cross-linkages. These methods do not appear to be of practical value, since during the reaction hydrogen chloride is evolved and in order to remove this acid the nitrocotton would have to be stabilized again. Besides, there exists the undesirable possibility of producing with great ease a substance so thoroughly cross-linked that it is insoluble in organic solvents. The processes also appear to be rather expensive as large enough quantities of cross-linking agents are required.

Another interesting cross-linking was obtained by Kreshkov, Guretskii and Andryanov [39a]. They reacted tetra-alkoxysilanes with nitrocellulose to obtain a reaction with free OH groups.



The product is highly resistant towards acids. It possesses high thermal resistance and good dielectric properties.

More important from the practical point of view is the discovery of Fordham, W. H. Marshall and Browne [40] that dihydroxydimethyl urea, commonly known

under the name of dimethylol urea, and also its ethers, were suitable agents for producing cross-linkages. The action of those substances is very slow, however. Thus the addition of about 0.1% of dihydroxydimethyl urea dibutyl ether to a low-viscosity solution of nitrocellulose in nitroglycerine produces the desired viscosity increase only after a week if kept at 60°C (Fordham and Browne [41]).

Among other substances capable of cross-linking di-isocyanates, e.g. hexamethylene di-isocyanate, $OCN-(CH_2)_6-NCO$, should be mentioned. It also reacts with free HO groups to form carbamic esters.

HYDROLYSIS AND DENITRATION

The general aspect of the problem of hydrolysis has been discussed already (p. 7). Here some particular points on hydrolysis of nitrocellulose will be briefly described.

Nitrocellulose, treated with different hydrolysing agents such as aqueous solutions of alkalis, does not yield cellulose and the corresponding metal nitrate, but a range of highly variable decomposition products of cellulose as well as of inorganic substances.

Different authors have isolated definite compounds from the products of alkaline hydrolysis of nitrocotton. Wolfrom *et al.* [42] enumerate the compounds that are produced by hydrolysis of nitrocellulose in the presence of acids and bases:

inorganic nitrates and nitrites,
cyanides,
oxides of nitrogen (N_2O, NO, NO_2),
oxides of carbon (CO, CO_2),
ammonia,
organic acids: oxalic, malic, formic, glycolic, butyric, malonic, tartaric, trihydroxyglutaric, dihydroxybutyric, hydroxypyruvic, saccharic, tartronic.

Most of these products have been detected by the earliest investigators of nitrocellulose, such as Vohl [43], Béchamp [44], Hadow [45], Will [46] and M. Berthelot [47].

In the presence of solid sodium hydroxide the reaction can proceed so quickly and violently that it can bring about ignition of the nitrocotton.

The most extensive quantitative examination of the alkaline decomposition of nitrocellulose has been carried out by Kenyon and Gray [48].

Nitrocellulose can undergo hydrolysis by moisture at temperatures above room temperature, or even at room temperature as discussed in more detail below in the chapter on the decomposition of nitrocotton.

Nitrocellulose dissolves in concentrated sulphuric acid, at the same time decomposing slowly, losing nitric acid to form a sulphuric ester.

In concentrated nitric acid, sp. gr. 1.52, it dissolves on warming (80 to 90°C). As the result of the prolonged action of more dilute nitric acid, specific gravity 1.41, a partial denitration and formation of oxycellulose occurs.

In order to achieve complete hydrolysis of nitrocotton, and to recover cellulose as unimpaired as possible, nitrocellulose is subjected to the action of sodium or ammonium hydrosulphide according to the equation:

$$C_6H_8O_3(ONO_2)_2 + 2NaHS \longrightarrow C_6H_{10}O_5 + 2NaNO_2 + 2S$$

$$2NaHS + 2S \longrightarrow Na_2S_3 + H_2S$$

The nitrate groups are removed and reduced to sodium nitrite. The reaction is of the first order.

This method of denitrating cellulose nitrate was widely used industrially to regenerate cellulose from the first (nitrocellulose) artificial fibre (Chardonnet [49]).

Rassow and Dörr [50] examined the influence of different denitrating agents and concluded that a denitration performed with the aid of KHS or NH_4HS proceeded more rapidly in an alcoholic solution that in an aqueous one. According to these investigators the denitration is never complete, some nitrate groups remaining unchanged. These may be detected by treating the substance with diphenylamine dissolved in concentrated sulphuric acid. A blue colour demonstrates that owing to the presence of nitrate groups nitric acid and nitrogen oxides are evolved under the influence of sulphuric acid.

To explain the mechanism of denitrating nitrocotton by means of hydrosulphides the reactions (17) and (18) have been proposed by Nadai [51] (see p. 9). The reaction was also studied by Merrow, Cristol and Van Dolah [52] (see p. 9, reactions (15) and (16)).

During the reduction, nitrite ions and polysulphides are produced. The hydrolysis reaction (17) is rather slow, if performed in a medium of alkaline hydroxides alone. It can proceed considerably more rapidly if carried out in the presence of HS ions (18).

According to a statement of Oldham [53] nitrocellulose can be denitrated by reduction with iron or an iron–zinc mixture in an acetic acid solution.

It has been demonstrated by the work of numerous investigations that regenerated cellulose may contain 0.5–2.0% of nitrogen. Yield of the denitration reaction amounts to 90–96%.

During denitration cellulose is also degraded to some extent. This is probably the result of oxidation–reduction processes. Rogovin and Shlakhover [54] and Staudinger *et al.* [55] have established the average length of a regenerated cellulose chain-molecule to be appreciably shorter than the length of a nitrocellulose chain.

Cellulose trinitrate, 13.8% N, undergoes rapid denitration at room temperature when treated with dry pyridine. Segall and Purves [55a] have stated that in the presence of hydroxylamine the course of the reaction is changed: one molecule of N_2 is produced and a highly polymerized fibre-like dinitrate with a number of nitro groups 1.7 is formed. During this reaction denitration without degradation takes place.

The dinitrate produced is characterized by its solubility in organic solvents

as well as by a relatively high resistance to alkalis. The NO_2 groups of this compound are attached in the positions 3 and 6. This has been determined by the following series of reactions:

$$\text{Dinitrate} \xrightarrow[\text{NaOH } 30\%]{(CH_3)_2SO_4} \text{Mono-O-methylcellulose dinitrate} \xrightarrow[NH_4HS]{\text{denitration}}$$

$$\longrightarrow \text{Mono-O-methylcellulose} \xrightarrow[5°C(16\text{ hr})]{H_2SO_4\ 72\%} \text{2-O-methylglucose} \qquad (5)$$

Hence the O-substituents (NO_2 groups) are placed in positions 3 and 6, so that the substance is a 3,6-cellulose dinitrate.

Nitrocellulose with a nitrogen content of 13.0 up to 13.9% has been reduced by Soffer, Parrotta and di Domenico [56] by means of lithium-aluminium hydride in a tetrahydrofuran medium. A yield 90–95% of considerably degraded cellulose was obtained.

X-Ray investigations on regenerated cellulose have shown that its structure approximates to the constitution of hydrated cellulose, i.e. mercerized cotton.

An interesting chemical exchange process occurs when nitrocellulose is boiled with sodium iodide: the primary nitrate groups ($-CH_2ONO_2$) are substituted by iodomethyl groups ($-CH_2I$). On treating high-nitrated cellulose (13.2% N) oxidation processes accompany this reaction, but these side reactions do not occur with low-nitrated cellulose. Murray and Purves [57] have studied these chemical reactions using nitrocellulose containing 2.5–9% N and established that at least half the O-nitro groups are bonded to primary alcoholic groups.

OTHER REACTIONS

Among other characteristic reactions of nitrocellulose worthy of notice is the transesterification of cellulose nitrate performed by means of acetic anhydride. In this way cellulose mononitro-diacetate was obtained (Berl and Smith [58]).

Clément and Rivière [59] also reported that cellulose acetate or a mixed ester — a nitrate–acetate — can be obtained by reacting cellulose nitrate with acetic anhydride, acetic acid, and sulphuric acid. According to more recent contributions, e.g. Wolfrom, Bower and Maker [60], the reaction should be performed as follows: Cellulose nitrate is dissolved in the cold in a little sulphuric acid and acetic anhydride, the surplus of acetic anhydride is then hydrolysed also in the cold, and cellulose acetate is extracted with a suitable solvent, such as chloroform. Other methods of acetylating nitrocellulose consist in reduction, for instance with zinc and hydrogen chloride, which entails denitration of the ester, followed by acetylation with acetic anhydride. All these reactions are carried out in the same vessel. Further, it is possible to synthesize mixed esters, cellulose nitrate–acetates, by subjecting cellulose to the action of a mixture that includes nitric acid, acetic acid and acetic anhydride in the presence of sulphuric acid (Krüger [61]). The use of a large amount of nitric acid favours the formation of nitrocellulose only. Mixed esters are formed

when the concentration of nitric acid in the mixed acid is low. Danilov *et al.* [62] have reached a similar conclusion.

Amination of cellulose is a relatively new reaction (Scherer and Feildt [63]). It occurs if nitrocellulose in liquid ammonia is exposed to the action of sodium or potassium amide, according to the equation:

$$C_6H_8O_3(ONO_2)_2 + NaNH_2 \longrightarrow \begin{matrix} OH \\ \diagup \\ C_6H_8O_3 \\ \diagdown \\ NH_2 \end{matrix} + NaNO_3 \qquad (6)$$

Only half the nitrate groups present in cellulose dinitrate is substituted by amine groups, the other half undergoing hydrolysis.

Aminocellulose is a reddish-yellow hygroscopic powder that dissolves readily in water. It can be diazotized and coupled with phenols to yield reddish dyes.

However, aminocellulose should be considered as a derivative of highly degraded cellulose, and could hardly be called a cellulose derivative.

The same objection should be raised to aminocellulose acetylide of Scherer and Saul [64].

DECOMPOSITION OF NITROCELLULOSE

Early experiments (1861–67) devoted to the decomposition of nitrocellulose were carried out by de Luca [2], who was the first to perceive that the decomposition rate of unstable guncotton increased more rapidly in moist air. He also found that decomposition was accelerated under the influence of the sunshine. Unstable guncotton stored in a dark room and at a low temperature, decomposed more slowly.

According to the classical work of Abel [3] the instability of nitrocotton samples is caused not so much by the tendency of nitrocellulose to decompose, as by the presence of certain impurities. Abel showed that the purest nitrocellulose was so resistant to decomposition by heating that it could withstand the action of a temperature between 65 and 100°C even for several months. He also demonstrated that low-nitrated cellulose added to guncotton does not exert an adverse effect on the latter's stability and its capacity to withstand the heat test.

Vieille [65] supposed a lower nitrated cellulose to be less stable than a higher nitrated one. This suggestion arose from considering the behaviour of differently nitrated cellulose towards hydrochloric acid. According to Vieille a low-nitrated cellulose is attacked by hydrochloric acid even in the cold, collodion cotton undergoes decomposition by hydrochloric acid only on boiling, whilst prolonged boiling is necessary to remove all the nitrogen from a guncotton containing 13% of nitrogen, and to convert it into nitrogen oxides.

The phenomenon described by Vieille seems to have no direct connection with the chemical stability of nitrocellulose, in the usual sense of this term, meaning the capacity of a substance to endure long storage, but appears to be limited to the

capacity of being hydrolysed under exactly determined conditions, i.e. in hydrochloric acid. However, under these conditions cellulose itself does not manifest any chemical stability: it is readily dissolved in hydrochloric acid, being simultaneously hydrolysed to yield glucose. In respect of this property, an incompletely nitrated cellulose differs from cellulose less than a high nitrated product, hence it also retains a high sensitivity to the hydrolytic action of hydrochloric acid.

If the temperature of nitrocellulose is raised steadily, e.g. at the rate of 5°C/min, an explosive decomposition takes place at a temperature of 180–185°C. With a lower rate of heating the temperature of decomposition is lower: about 165°C.

The decomposition reaction of cellulose nitrate brought about by heating is an autocatalytic process. According to the investigations of Will (p. 299) completely pure nitrocellulose undergoes decomposition at a constant rate, if the decomposition products are removed, otherwise the reaction accelerates owing to the activity of acid products ($N_2O_4 + H_2O$). Below the temperature of initiation decomposition is relatively slow. In the case of well stabilized nitrocotton it ceases at room temperature or a slightly higher one (30–35°C). An insufficiently stabilized nitrocellulose, that contains unstable cellulose esters or traces of acids, can decompose at normal storage temperature, finally producing an explosive decomposition in the same way as that resulting from heating.

From experiments on the decomposition of nitrocotton (13.1% N) within the temperature range 126.5–157°C, Will formulated an equation from which the decomposition of nitrocellulose can be estimated:

$$\log_{10} N = a + b \times 0.9932^t$$

where: N — milligrams of nitrogen evolved from 2.5 g of nitrocellulose in period of 15 min, t — temperature (°C), a, b — coefficients: $a = 8.84$, $b = -22.86$.

Miles [15] has applied the Arrhenius equation to the numerical data of Will and calculated the following values:

activation energy $E = 46.2$ kcal/mole

the constant $\log_{10} B = 24.68$

It is noteworthy that in more recent studies on nitrocellulose decomposition (Wilfong, Penner, Daniels [66]) similar results and values for the activation energy have been obtained, namely $E = 46.67$ kcal/mole in the temperature range 84 to 162°C. R. D. Smith [67] has examined the thermal decomposition of nitrocotton of 11.8% N in such high-boiling substances as chlorodinitrobenzene, nitronaphthalene, benzophenone, within the temperature range 165–200°C and determined the values:

$$E = 43.0 \text{ kcal/mole}, \quad \log_{10} B = 18.0$$

Will and other contemporary workers assumed that nitrogen evolved during the thermal decomposition of nitrocotton occurred chiefly as nitrogen oxide. On the

contrary nitrogen dioxide is produced in relatively inappreciable quantities. R. Robertson and Napper [68] used Will's apparatus to decompose nitrocotton in an atmosphere of carbon dioxide. They examined the decomposition products spectrographically and established that over 50% of the nitrogen evolved from nitrocellulose is produced in the form of nitrogen dioxide.

The proportion of nitrogen dioxide among the decomposition products varies according to the experimental conditions. Thus on maintaining a temperature of 135°C for 60 hr the nitrogen content was decreased from 13 to 8.7% N. The evolution of nitrogen was more or less constant at *ca.* 0.72 mg per hour per 1 g of nitrocellulose. At the beginning nitrogen dioxide represented as much as 54% of the total quantity of nitrogen, while near the end it was scarcely 8%.

In view of those experiments some results reported by later authors who did not find NO_2 among the thermal decomposition products of nitrocellulose should be subjected to revision. There is in fact, a serious controversy concerning this question as shown in the following paragraphs.

Koehler and Marqueyrol [69] investigated the products of nitrocellulose decomposed under pressure. The decomposition products were removed in order to avoid the possibility of starting side reactions and to preclude any catalytic action by the decomposition products on the nitrocellulose. It has been stated that the composition of the gases evolved during decomposition is almost independent of the temperature and this is compatible with the data reported by Robertson. However, the composition of the products differs from that found by Robertson. These are as follows (omitting the water formed):

NO	62.0%
CO_2	20.0%
CO	8.5%
N_2O	3.8%
N_2	6.0%

According to Goujon [10] heating nitrocotton in a carbon dioxide medium causes the nitrogen to evolve chiefly in the form of NO_2 and NO. In addition some N_2 and N_2O are produced. Hydrogen is evolved mainly as H_2O, carbon as CO_2 and to a smaller extent as CO. Traces of hydrocarbons are also formed.

If decomposition takes place with access to air, nitrogen oxide is, of course, converted to nitrogen dioxide. A large proportion of the latter is re-absorbed by nitrocellulose and hastens its decomposition, particularly in the presence of moisture, as it reacts as nitrous and nitric acids.

The researches of A. Sapozhnikov and Borisov [70] and of A. Sapozhnikov and Yagellovich [71] were devoted to a study of the evolution of gases during thermal decomposition of guncotton in air. As shown in the graph (Fig. 114) the quantity of gaseous products evolved is dependent on the temperature of heating.

The loss of weight and the volume of gases evolved from 1 g of guncotton are listed in Table 65.

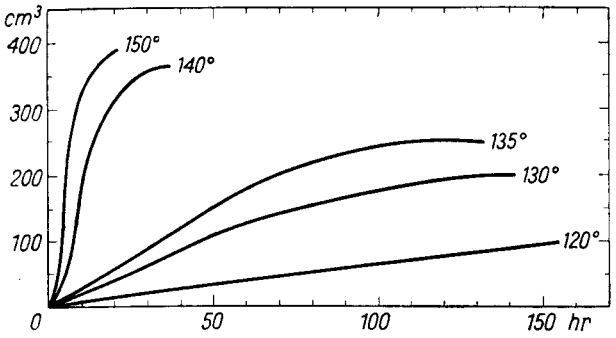


FIG. 114. Gas evolution from nitrocellulose at different temperatures (Sapozhnikov *et al.* [70]).

TABLE 65

THE EFFECT OF HEATING ON NITROCELLULOSE DECOMPOSITION

Temperature of heating °C	Time of heating hr	Volume of developed gases cm³	Loss of weight %	Loss of nitrogen %
125	150	162	49.7	64
135	150	236	61.8	83
140	40	310	66.5	91
150	20	325	70.2	98

On the basis of gas analyses the following gaseous decomposition products were calculated by Sapozhnikov and Borisov:

for a temperature of 125°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 2.5CO_2 + 1.60CO + 1.98NO + 2.52N_2 + 14.5H_2O \quad (7)$$

for a temperature of 135°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 5.03CO_2 + 2.10CO + 2.93NO + 3.04N_2 + 14.2H_2O \quad (8)$$

for a temperature of 140°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 6.22CO_2 + 3.20CO + 5.18NO + 2.70N_2 + 9.6H_2O \quad (9)$$

for a temperature of 150°C:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 6.27CO_2 + 3.58CO + 5.37NO + 2.70N_2 + 8.0H_2O \quad (10)$$

Hence at higher temperatures nitrogen is removed from the nitrocellulose almost completely.

Vandoni [72] has reported that at 108.5°C guncotton nitrogen is evolved into the atmosphere mainly as nitrous oxide. He has determined the percentage proportion of nitrogen compounds in the decomposition products as follows:

NO	1.89%
N_2O	13.79%
N_2	9.03%

plus: 63.61% of CO_2, 10.16% of CO, 1.52% of CH_4.

Vandoni has also examined the decomposition produced by treatment with water at 130°C of high-nitrated guncotton, 14% N, and the decomposition products of nitrocellulose of 12% N evolved when treated at 50°C with dilute (25% HNO_3) nitric acid.

The composition of the gases in both experiments was:

temperature	N_2O	NO	N_2	CO_2	CO	CH_4
130°C	26.57	1.05	3.96	64.43	2.70	1.29
50°C (with HNO_3)	15.39	32.33	5.01	42.13	5.24	0.0

A probable mechanism for the thermal decomposition of nitrocellulose has been suggested by Desmaroux [73] who assumed the occurrence of three types of decomposition reaction:

(1) hydrolysis of ester (—ONO_2) groups;
(2) hydrolysis of linkages between particular glucose units;
(3) intermolecular oxidation of particular anhydroglucose rings, while during the oxidation of one ring the neighbouring units may remain intact.

Desmaroux [73a] followed the decomposition of nitrocotton kept at a temperature of 132°C and established that the reaction types (1) and (3) predominated. Only $\frac{1}{3}$–$\frac{1}{2}$ of the substance broke down by the hydrolysis of ester groups. Desmaroux also determined the loss of weight of the sample so as to compare it with the loss of nitrogen. The weight loss of the nitrocellulose calculated on the basis of the nitrogen lost is 3–12 times smaller than the total weight loss, as seen from the data in Table 66.

TABLE 66

THERMAL DECOMPOSITION OF NITROCELLULOSE (ACCORDING TO DESMAROUX [73a])

Nitrogen content of nitrocellulose %	Sample heated for 24 hr (at 132°C)			Sample heated for 32 hr (at 132°C)		
	P	*N*	*R*	*P*	*N*	*R*
13.38	0.131	12.94	5.4	0.093	12.86	3.3
12.32	0.154	11.77	5.4	0.269	11.61	7.4
12.13	0.254	11.58	8.6	0.372	11.40	10.0
11.71	0.325	11.07	7.9	0.512	10.86	12.2

The symbols used in Tables 66 and 67 indicate:

P — the loss in weight of 1 g of nitrocotton, *N* — the nitrogen content (in per cent). *R* — the $P/(N_0—N)$ ratio, where $N_0—N$ is the loss in weight of 1 g substance calculated from the loss of nitrogen.

Lower nitrated types of nitrocotton lose their nitrogen to a smaller degree than higher nitrated types, as would be expected.

In addition to the three main types of reaction involved in nitrocellulose decomposition, the author assumes that secondary reactions also occur originating in the chemical combination between oxides of nitrogen and water vapour to produce nitric and nitrous acids, which in turn react with the nitrocellulose. By heating nitrocotton with dilute nitric acid at 40°C, Desmaroux found in this instance that hydrolytic and oxidation reactions predominate, causing a weight loss of $\frac{1}{2}$–$\frac{1}{4}$ of the total loss (see Table 67).

TABLE 67

THERMAL DECOMPOSITION OF NITROCELLULOSE (ACCORDING TO DESMAROUX [73a])

Nitrogen content of nitrocellulose	HNO_3 %	Sample heated for 24 hr (at 40°C)			Sample heated for 72 hr (at 40°C)		
		P	*N*	*R*	*P*	*N*	*R*
13.38	25	0.012	13.25	1.63	0.014	13.12	0.97
	45	0.058	12.60	1.39			
12.13	25	0.00	11.93	—	0.029	11.72	1.42
	45	0.265	10.09	2.76			

In one of the experiments, a denitration of the nitrocotton without any perceptible loss of weight was observed. This showed that nitrocellulose of low nitrogen content (12.13%), was denitrated with ease, and is in good agreement with Vieille's observation (mentioned above), that lower nitrated nitrocellulose was more easily decomposed when boiled with an acid. Gelernter *et al.* [96] examined the decomposition of nitrocellulose (10.8–11.8% N) labelled with ^{15}N at 157°C and found the secondary ONO_2 groups less stable than those of C_6.

Decomposition of nitrocellulose by light. The effect of sunlight and of ultra-violet light on the viscosity of nitrocellulose solutions has already been discussed (see p. 275). However, the irradiation of nitrocellulose causes not only a decrease in the degree of polymerization but also a decomposition involving denitration. D. Berthelot and Gaudechon [74] followed the effect of irradiating nitrocotton by ultra-violet light, and found among the decomposition products CO, CO_2, N_2 and oxides of nitrogen. A. Kraus [75] reported that nitrocellulose containing 11.74% of nitrogen was denitrated to 10.81% by irradiation for 48 hr.

T. Urbański and Malendowicz [76] have examined the rate of decomposition of nitrocellulose by ultra-violet light. The results showed (T. Urbański [77]) that nitrocellulose of 13.3% N undergoes decomposition expressed by an exponential equation, whereas lower nitrated nitrocotton, 11.9% of N, decomposes approximately in accordance with a linear function. Somewhat discordant results were published by Oguri, Takei and Fujita [78] who reported the fall in nitrogen content of nitrocellulose to be 1.0% N, after 3 hours irradiation, and 1.95% N after 8 hr.

G. G. Jones examined the effect of ultra-violet light of different, selected wave-

lengths on nitrocellulose, containing 12.2% N, dissolved in methanol or in ethyl acetate.

Radiation of 253.6 mμ wave-length especially is capable of reducing the viscosity of nitrocellulose solutions. Radiation of 366 mμ wave-length has practically no influence on the viscosity. Nitrogen content was decreased in both cases. With 366 mμ radiation applied under specific experimental conditions, the nitrogen content was reduced after 48 hr from 11.85 to 11.68%.

It is also known that nitrocellulose or nitrocellulose film grows yellow as a result of prolonged exposure to sunshine.

Nitrocellulose (11.8%N) has been decomposed by the action of intense γ-radiation and its microstructure (as shown by X-rays) was entirely disrupted [95].

Other factors. It has been stated many times that some kinds of moulds, e.g. *Aspergillus*, can grow on wet nitrocotton. The first systematic enquiries in this field were made by Bokorny [79]. He found that moulds could grow in a medium comprising an aqueous solution of mineral salts, in which nitrocellulose was suspended. Bokorny suggested that nitrocellulose provided the mould with essential carbon, and perhaps nitrogen. Hence, anxiety was aroused (e.g. Sy [80]) concerning the possibility that denitrifying bacteria might bring about the decomposition of nitrocotton. It was established however by further investigations (Malenković [81], Jacqué [82]), that only the mineral salts dissolved in the water were being utilized by the moulds and by the micro-organisms, which cannot bring about the decomposition of nitrocellulose. However they can produce various organic substances, e.g. acids, which in turn may have an adverse effect on the stability of nitrocellulose and other nitric esters. It has been established that nitrocellulose can be protected against moulds by the addition of a small amount of corrosive sublimate. This technique was used for a time at the beginning of the current century, particularly for nitrocotton exported to tropical countries. Later the method was abandoned for the corrosive sublimate interfered with the heat test with potassium iodide–starch making it difficult to detect inadequate stabilization of the nitrocellulose (the question will be discussed in detail in Vol. III).

EXPLOSIVE PROPERTIES OF NITROCELLULOSE

The equation of decomposition and the physical constants reported by Kast [83] are quoted below. They refer to guncotton of 13.1% N:

$$2\begin{cases} C_{24}H_{29}O_9(ONO_2)_{11} \\ C_{24}H_{30}O_{10}(ONO_2)_{10} \end{cases} = 36CO_2 + 47CO + 4CH_4 + 39H_2O + 2C_2H_2 + 3HCN + 3.5H_2 + 18.5N_2 + 2NH_4HCO_3$$

Heat of explosion	1025 kcal/kg
Volume of gases evolved	$V_0 =$ 765 l./kg
Temperature	$t =$ 3100°C

The decomposition equation for the same guncotton containing 16% of water, has the following values:

$$2\left\{\begin{matrix}C_{24}H_{29}O_9(ONO_2)_{11}\\ C_{24}H_{30}O_{20}(ONO_2)_{10}\end{matrix}\right. + 48H_2O = 41CO_2 + 37CO + 5CH_4 + 63H_2O + C_2H_2 + HCN + 7.5H_2 + 15.5N_2 + 10NH_4HCO_3 + 875 \text{ kcal/kg}$$

$$V_0 = 720 \text{ l./kg}$$
$$t = 2260°C$$

Guncotton such as the above, in a dry state, compressed to a density of 1.30 g/cm^3 demonstrated a detonation rate of 6300 m/sec, and an expansion in the lead block of 375 cm^3, while guncotton with 16% of water content detonated with a rate of 6800 m/sec, and produced an expansion in the lead block of 280 cm^3.

Milus [84] investigated the explosive decomposition of nitrocotton with different nitrogen content and obtained experimental data which he used to calculate the values tabulated below (Table 68).

Taking into account earlier experiments, Roux and Sarrau [85] have estimated the heat of explosion of guncotton to be 1056 kcal/kg, a value compatible with those

TABLE 68

EXPLOSIVE DECOMPOSITION OF NITROCELLULOSE (AFTER MILUS [84])

	Nitrogen content of nitrocellulose, %				
	12.62	13.0	13.15	13.2	13.45
Heat of explosion					
cal/g (H_2O liquid)	973	1025	1046	1055	1096
cal/g (H_2O vapour)	865	925	946	955	955
Volume of gases:					
V_0 cm^3/g (H_2O liquid)	900	880	874	868	857
Composition of the gas: (H_2O liquid)					
CO_2	21.2	23.8	24.3	24.4	27.0
CO	45.9	43.9	43.7	43.5	41.0
H_2	18.7	17.3	16.7	16.5	16.1
CH_4	0.4	0.4	0.4	0.4	0.3
N_2	13.8	14.6	14.9	15.1	15.6
Temperature of explosion:					
t, °C	2840	3025	3095	3130	3245
Composition of gases calculated for respective temperature of explosion:					
CO_2	10.5	13.9	14.3	14.4	16.0
CO	43.8	40.8	40.5	40.2	38.6
H_2	9.5	9.6	9.2	9.0	7.9
N_2	11.1	11.7	11.9	12.1	12.5
H_2O	25.1	24.0	24.1	24.3	25.0

quoted above. According to Taylor and Hall [86] the heat of explosion for nitrocelluloses containing 12.1–12.3% N varies from 883.5 to 929.5 kcal/kg. The discrepancies are undoubtedly attributable to differences in the conditions of experiments, i.e. by the formation of different explosion products. Taylor and Hall report that the heat of explosion of nitrocotton in calories per gramme (Q) for constant volume and liquid water at 0°C, may be expressed as a linear function of the nitrogen content:

$$Q = 144.9\,N - 850.3$$

The heat of combustion (experimental values) and the heat of formation (calculated) by Tomioka [87] and Lenze *et al.* [88] for nitrocelluloses of different nitrogen content are listed in Table 69.

TABLE 69

HEAT OF COMBUSTION AND HEAT OF FORMATION OF NITROCELLULOSE

Nitrogen content %	Heat of combustion kcal/kg	Heat of formation kcal/kg	Author
7.66	3071	958.9	Tomioka [87]
10.14	2717	804.1	Tomioka [87]
11.06	2612	742.3	Tomioka [87]
12.45	2434	645.2	Tomioka [87]
12.88	2390	616.5	Tomioka [87]
13.53	2236	594	Lenze, Metz and Rubens [88]
13.58	2286	568.7	Tomioka [87]
13.92	2239	513	Lenze, Metz and Rubens [88]
14.12	2208	504	Lenze, Metz and Rubens [88]

Values found for the heat of formation of nitrocellulose by Taylor and Hall are lower than those given in Table 69.

Recently, Jessup and Prosen [89] have examined the heat of combustion of cotton cellulose and wood pulp cellulose, and of their nitrates. The data for di- and trinitrate are higher than those of Taylor and Hall, and approximate to the

TABLE 70

HEAT OF FORMATION OF NITROCELLULOSE (AFTER TAYLOR AND HALL [86])

Nitrogen content %	Number of nitro groups in relation to C_6	Molecular weight of a C_6 unit	Heat of formation	
			$-\Delta H_f$ kcal/mole	kcal/kg
10	1.71	238.8	181.4	759.6
11	1.97	250.6	174.0	694.3
12	2.26	263.8	165.7	628.1
13	2.58	278.3	156.5	562.3
14	2.94	294.6	146.3	496.6

values published by earlier authors (Tomioka [87], Lenze, Metz and Rubens [88]). No essential difference has been found between the values for cotton and wood pulp cellulose.

Jessup and Prosen deduced for nitrocotton an equation that expresses the heat of combustion and the heat of formation as functions of the nitrogen content:

$$-4176.70+14.126\,f' \text{ cal/g of nitrocellulose and}$$
$$-5896.88+21.178\,f' \text{ cal/g of nitrocellulose, respectively,}$$

where f' — the mass of nitrogen in nitrocellulose calculated for the mass of nitrocotton = 1.0. The formula is valid for f' values from 0.115 to 0.135

Nitrocellulose is very inflammable. It burns extraordinary readily though without detonating. Explosion can occur on burning large amounts of guncotton particularly in a confined space. The rate of burning depends on the type of guncotton, i.e. on the degree of nitration, the degree of fineness etc. as well as on the moisture content. Dry nitrocellulose is extremely inflammable and very dangerous. A higher fineness reduces the inflammability by increasing the loading density under given pressure. Increase in nitrogen content on the other hand increases the inflammability.

Andreyev [90] has established the linear rate of burning for guncotton and collodion cotton under different pressures:

For guncotton No. 1
density 0.56–0.68 g/cm^3, under pressures (p) of 3–12 kg/cm^2 the rate of burning is defined by the equation

$$U = 0.0907+0.0405p$$

For collodion cotton
density 0.47–0.54 g/cm^3, under pressures in the range 4–30 kg/cm^2

$$U = 0.0710+0.0162\,p$$

According to Andreyev and Polyakov the rate of burning under higher pressures, e.g. over a few kg/cm^2, increases more slowly and follows a nearly straight-line law (Fig. 115).

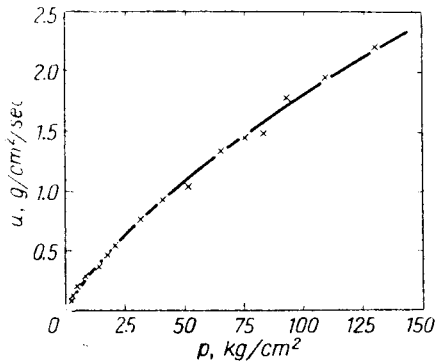


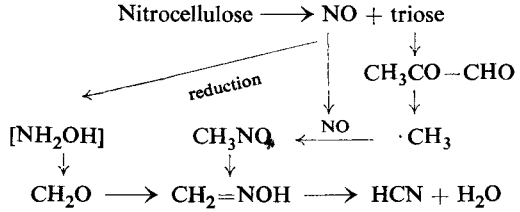
FIG. 115. Rate of burning of nitrocellulose under different pressures according to Andreyev [90].

Experiments on burning nitrocellulose (deflagration and explosion) were carried out in World War II by Rideal and A. J. B. Robertson [91]. One interesting observation they made was that nitrocotton heated for a long time at 200°C under a pressure of 50 mm Hg liquefied shortly before the explosion. Nitrocellulose has been known to melt while being stabilized in an autoclave at an elevated temperature, since it overheats if there is too little water in the autoclave (on melting nitrocellulose, see p. 242).

Recently extensive investigations on burning nitrocellulose under reduced pressures have been carried out by Wolfrom *et al.* [42, 92] who have described their results in a series of papers. Nitrocellulose of 12.6–13.2% N was examined. It was ignited under pressures of 2–3 mm Hg or 200 mm Hg.

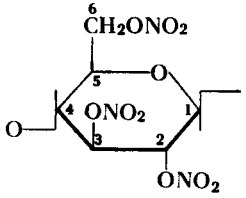
At the lowest pressures investigated, a white fragmented oxycellulose nitrate (9% N) was isolated in good yield (*ca.* 40% by weight). The yield of this material decreased rapidly with increasing pressure, and a liquid mixture containing formic acid, formaldehyde, glyoxal and HCN was obtained. The cyanide ion is detectable immediately following ignition, and disappears soon after, simultaneously with the disappearance of compounds with a carbonyl group, such as formaldehyde and glyoxal. This is probably due to the formation of cyanhydrins which have been found in the decomposition products.

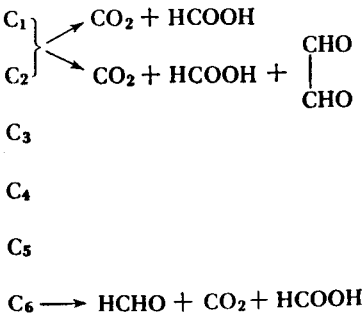
Intermediate formation of a triose (identified as phenylosazone) was also proved by the authors and the following sequence of reactions is suggested:



(11)

In the last paper of Wolfrom, Shafizadeh *et al.* [93] nitrocellulose labelled at C_1 and C_2 with ^{14}C was used for the experiments. This led to the conclusion that C_1 gives mainly CO_2 and lesser amounts of formic acid and glyoxal (the latter from C_1 and C_2) and that the major product from C_6 is formaldehyde with lesser amounts of formic acid and CO_2:





As a safety precaution nitrocellulose intended to be transported should always contain 25–30% of water. Guncotton rich in nitrogen will, however, ignite even if the water content exceeds 40%, but it is difficult to raise the moisture content above 30%, since nitrocellulose is not capable of absorbing more water.

Collodion cotton used industrially for lacquers, celluloid and such like, can be transported after being wetted with ethyl, propyl or butyl alcohol the choice depending on which alcohol is to be used as a component of the solvent for the nitrocellulose in question.

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CHAPTER XII

NITRATION OF CELLULOSE

NITRATION WITH NITRIC ACID

THE first attempts to esterify cellulose by means of nitric acid consisted in treating cellulose with the acid without any dehydrating agents. Vieille [1] discovered in 1882 that on nitration with nitric acid alone the rate of reaction and the nitrogen content of the nitrocellulose increased as the concentration of HNO_3 was increased:

concentration of HNO_3, %:	77.3	80.8	83.5	87.0	89.6	92.1	95.1
% N in nitrocellulose:	6.85	8.07	8.78	10.33	11.53	12.23	12.68

Attempts to obtain nitrocellulose containing more than 12.7% of nitrogen failed. When acid diluted below 77% was used partial dissolution of the product occurred. As an explanation for this, Vieille suggested that the soluble substances represented products which were hydrolysed or oxidized under the influence of the relatively dilute nitric acid. The reactions of hydrolysis and oxidation occur less readily the more concentrated the nitric acid, and the more hydroxyl groups are esterified. It also seems that nitrate groups counteract the side processes (such as oxidation).

A number of authors have shown that esterification can be carried out with nitric acid of over 65% concentration. Sixty five per cent acid, of specific gravity 1.14, yields addition products with cellulose, as obtained by Knecht [2]. After removing the acid retained mechanically Knecht established that the addition compound contained nitric acid corresponding to 7.7% N. This is approximately equivalent to one NO_2 group for every anhydroglucose unit. Drowning the addition product in water causes nitric acid to split off. Knecht thought that it was an exceptionally labile nitrate. Häussermann [3] found it to be a rather unstable addition product. Champetier and Marton [3a] examined the ultra-violet reflexion spectrum of the Knecht compound. They found it contains a band 270–305 mμ which is not present in the spectrum of nitrocellulose. The authors considered that this supports the view that the Knecht compound is an individual substance differing from nitrocellulose.

Cellulose regenerated from the addition compound may demonstrate a certain degree of nitration, say 0.5–2.2% N. The properties of the compound are similar to those of hydrocellulose: glittering fibres, increased hygroscopicity, higher reactivity.

X-Ray investigations by Hess and Katz [4] suggest that the addition product is probably compatible with the formula $C_6H_{10}O_5 \cdot HNO_3$. The X-ray diagram of the compound is a characteristic one differing from that of cellulose. On the basis of their research these workers concluded that the addition compound was produced by the action of 86% nitric acid. According to Trogus [5] it is not out of question, that besides the product of composition mentioned above, another compound is formed consisting of cellulose and nitric acid hydrate: $C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$ (see below).

Moreover, there is some evidence that the addition compound is also formed as a transient product in the first stage of nitrating cellulose by means of a mixed nitric and sulphuric acid.

According to the experiments of Andress [6] the composition of the "Knecht compound" after being kept under reduced pressure for some time should be denoted by the formula $2C_6H_{10}O_5 \cdot HNO_3$. Andress has demonstrated that the compound produces a characteristic X-ray fibre diagram.

Later, Wilson [7] established that the composition of the compound after drying under a "high vacuum" is:

$$2C_6H_{10}O_5 \cdot HNO_3 \cdot H_2O$$

The product of absorption of nitric acid vapours by cellulose is according to Wilson not a Knecht compound, since it did not give the characteristic X-ray diagram although its chemical composition is approximately that of the Knecht compound.

Trogus [5] collected numerical data (Fig. 116) concerning the concentration of nitric acid to produce Knecht compound (*I*), nitration of cellulose expressed in terms of nitrogen content (% N) (*II*), freezing points of nitric acid–water solutions (*III*), and HNO_3 partial vapour pressure in nitric acid–water solutions (*IV*). The concentrations of HNO_3 in aqueous nitric acid that produce strong swelling or solution (*ca.* 80% HNO_3) of cellulose are also included. The diagram shows which factors play an important part in the formation of the Knecht compound and in the nitration of cellulose. It seems that the Knecht compound is formed when a mixture of almost equivalent quantities of the hydrates $HNO_3 \cdot H_2O$ and $HNO_3 \cdot 3H_2O$ acts on cellulose. The curve of nitration (*II*) follows a similar trend to the curve for the vapour pressure of HNO_3 (*IV*).

Andress and Rheinhardt [9] have discovered that cellulose swells in an aqueous solution of perchloric acid to produce the compound $2C_6H_{10}O_5 \cdot . HClO_4$ which also gives a characteristic X-ray diagram. Miles [8] has suggested that the composition of this substance is:

$$2C_6H_{10}O_5 \cdot HClO_4 \cdot H_2O$$

It is impossible to obtain nitrocellulose containing a high percentage of nitrogen by nitration with nitric acid alone. This is explicable by the fact that every concentration, even the strongest nitric acid, causes the cellulose fibres to swell, and thus hinders the diffusion of acid into the fibre mass. Attempts to nitrate cellulose by means of a mixture consisting of nitric acid and sulphuric acid have demon-

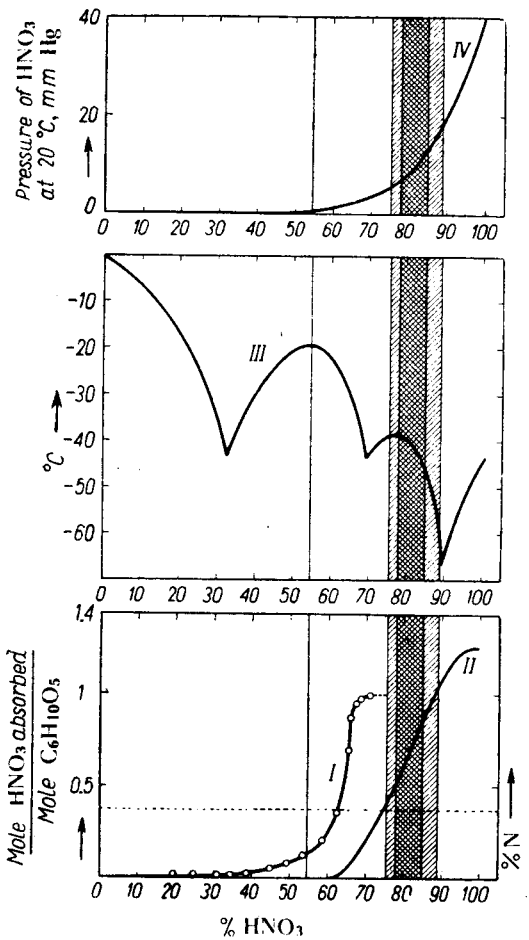


FIG. 116. Diagram by Trogus [5]: *I*—Formation of the addition (Knecht) compounds, *II*—Nitration of cellulose (in % N), *III*—Freezing temperature of HNO_3–H_2O solutions, *IV*—Partial vapour pressure of HNO_3 in aqueous nitric acid. Hatched area — strong swelling of cellulose fibre. Cross hatched area — solution of cellulose fibre in the acid.

strated, however, that the presence of sulphuric acid counteracts the swelling, and hence nitration can proceed more evenly.

On the other hand, attention should be drawn to the contribution of Miles and Wilson [10] who reported that nitric acid of 85% concentration causes the highest rate of nitration of all nitrating mixtures. An acid of this concentration produced a product containing 8.0% of nitrogen. Such an acid exerts a strong denitrifying effect on a higher nitrated nitrocellulose, as shown by the reversibility of the reaction of nitrating cellulose. Thus nitrocotton of 12.1% N is denitrated at a rate of 1.41% of N per hour at 20°C. Moreover, concentrated nitric acid of about 85% has been found to be most efficiently absorbed by nitrocellulose.

It is also possible to nitrate nitrocellulose which has already been partly pre-

nitrated. This principle has been used in the manufacturing process for nitrating nitrocellulose of 13.5% N by means of 100% nitric acid to obtain a product with 14.09% N (de Bruin and Witte [28a]). Another method consists in nitrating nitrocellulose by means of nitric acid vapours. A detailed description of such a process as applied in Germany will follow later (see p. 353).

Chédin and Tribot [11] have demonstrated that a 100% nitric acid which is capable of nitrating cotton linters up to 13.2% N can produce a higher nitrated product, if the gelatinized nitrocellulose after being converted into an amorphous mass by dissolving the product in acetone, precipitating by addition of water and drying, is further nitrated be means of nitric acid. This proceedure repeated several times makes it possible to increase the nitrogen percentage to as much as 13.7 to 13.8% N.

ABSORPTION OF NITRIC ACID BY CELLULOSE AND NITROCELLULOSE

The absorption of nitric acid is a phenomenon preceding nitration. Afterwards nitric acid is also absorbed by the nitrocellulose formed. This phenomenon has been examined under various conditions: e.g. the absorption of nitric acid in vapour form and the absorption of HNO_3 from pure nitric acid and from its solution respectively.

Wilson and Miles [12] have measured the absorption of nitric acid by treating with it nitrocotton of 13.8% N. Under a pressure of 4 mm Hg as much as 15% of HNO_3, was absorbed by this nitrocotton. Nitric acid is absorbed better by a lower-nitrated substance, just as the absorption of water vapour is easier in the case of lower-nitrated nitrocellulose. The maximum absorption has been established with nitrocellulose of 7% N. The amount of nitric acid absorbed by cellulose depends on its type. For native cellulose it amounts to about 25% by weight of the cellulose, and approaches 50% for mercerized cellulose. Such differences in the behaviour of different kinds of nitrocellulose indicates that swelling has an appreciable influence on absorption. Mercerized cotton which is more liable to swell simultaneously shows stronger absorption.

In another investigation by the same authors [13] the absorption of HNO_3 from aqueous solutions of nitric acid has been investigated. The absorption proceed most effectively, attaining about 50% with nitrocellulose of 13% N, if the latter is immersed in acid containing 80% of HNO_3, which has approximately the composition $HNO_3 \cdot H_2O$.

The relevent data are shown in the chart (Fig. 117) which depicts the absorption of HNO_3 and of water in the presence of vapours produced from nitric acid, 78 to 80% of HNO_3

The absorption of nitric acid from the nitrating mixtures is exceptionally interesting and important from the theoretical and practical point of view. It has long been known that nitric acid absorbed from a mixed acid is richer in HNO_3 than the nitrating acid itself.

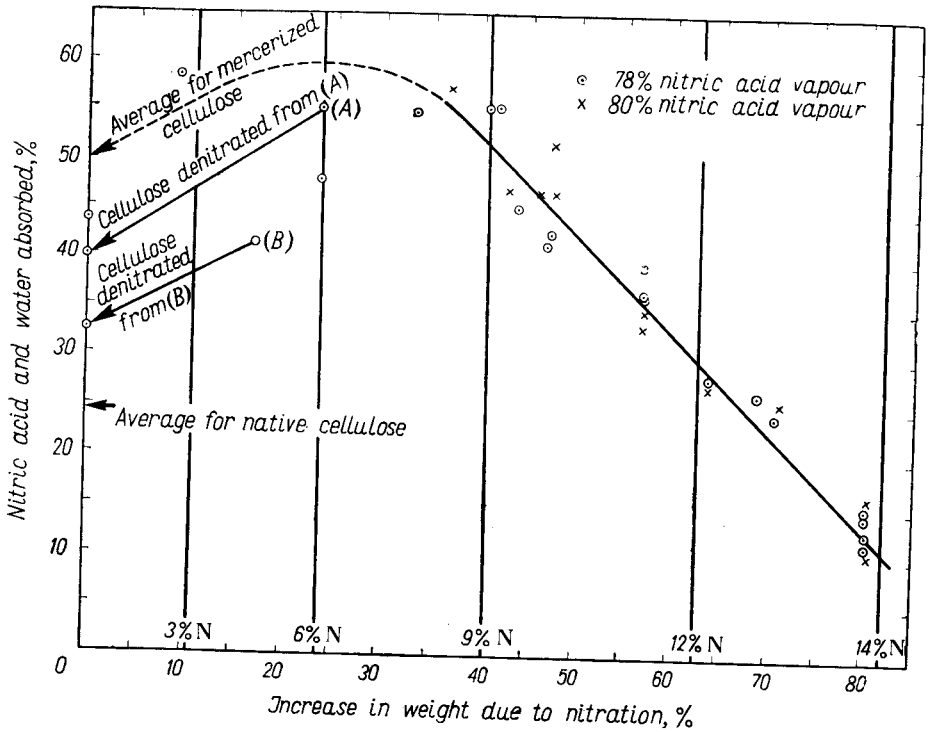


FIG. 117. Absorption of HNO_3 and water by nitrocellulose of 13.8% N (Wilson and Miles [13]).

The question of absorption of acids from their mixtures has been studied experimentally by Demougin and Bonnet [28], by Wilson and Miles [13] and more recently by Chédin [11]. The last author has provided clear experimental evidence that the nitric acid remaining in nitrocellulose after nitration has ended is present in two forms: as spent acid (after-nitration acid) of the same composition as the waste acid, and as nitric acid diluted to varying concentration by the water absorbed by the nitrocellulose fibres. The spent acid can be removed to some extent from the nitrocotton by squeezing it between rollers. By increasing the pressure from 150 to 550 kg/cm^2 the residue of this acid can be reduced from 121 to 45%. The chemical composition of the acid removed does not change appreciably with the wringing pressure. Nitric acid absorbed by nitrocellulose cannot be removed by mechanical operations such as, for instance, hydro-extraction.

Taking into consideration these experiments as well as later contributions (Chédin and Tribot [11]) Chédin has constructed a diagram (Fig. 118), the curves of which show:

(*1*) the chemical composition of mixed acids, from which a constant percentage of HNO_3+H_2O is absorbed;

(*2*) constant values of effective concentrations of nitric acid in the nitrating mixtures, expressed by the ratio

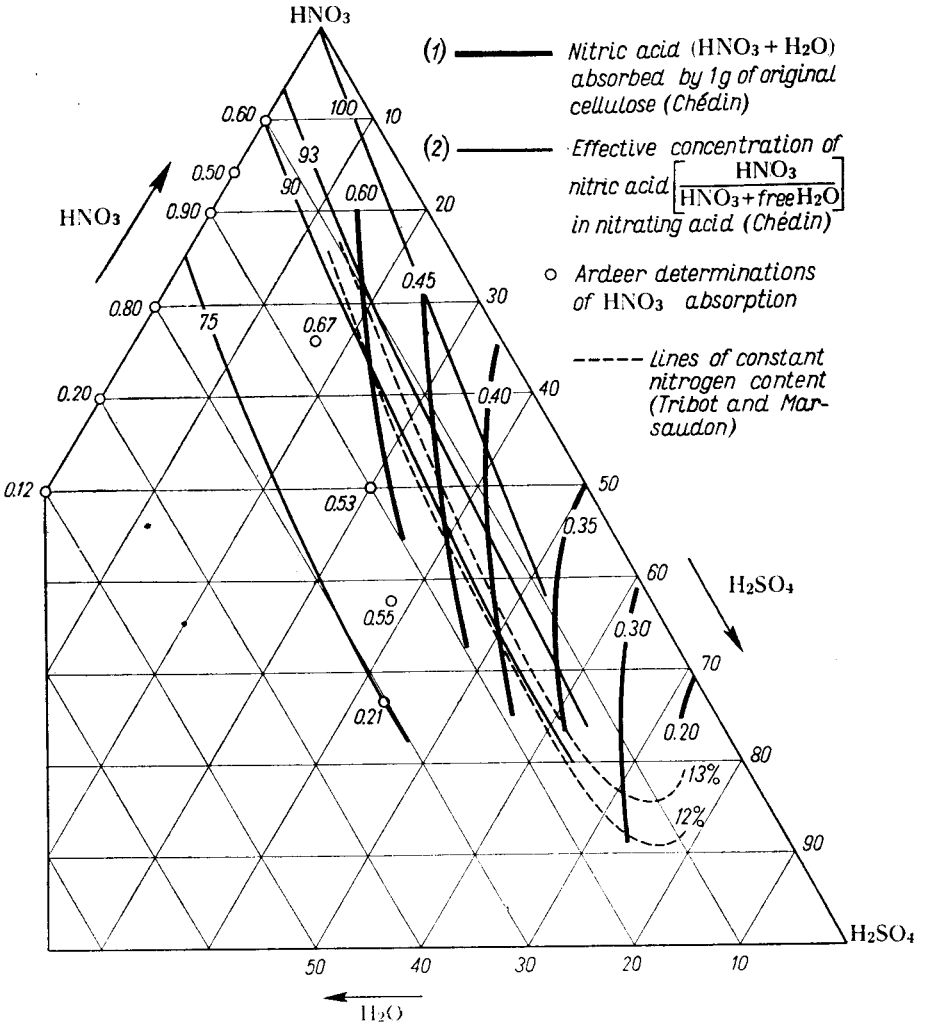


FIG. 118. Nitric acid absorption and effective concentration in mixed acid, according to Chédin and Tribot [11].

$$100\,\frac{HNO_3}{HNO_3 + H_2O}$$

The values (*1*) and (*2*) refer to absorbed nitric acid, the mixed acid retained in the nitrocellulose without being absorbed is neglected.

Thus the curves (*1*) and (*2*) give an idea of the absorption percentage ($HNO_3 + H_2O$), whereas the curves of series (*2*) are intended to illustrate the concentration of the absorbed acid.

For example nitrocellulose of 12% N prepared by nitration with a mixed acid containing 17% of H_2O and 25% of HNO_3 absorbed about 37% of nitric acid of *ca.* 90% concentration.

These observations are of importance in practice as they indicate that on separation of acid from the nitrocellulose, e.g. in centrifuges, the composition of the nitrating mixture retained in the product changes so that the concentration of the nitric acid is increased. As a result an additional "after-nitration" process can occur. Due to the small amounts of acids present in the product, the heat developed during after-nitration can raise the temperature of acid nitrocotton sufficiently high to bring about inflammation or even explosion.

The tendency of nitrocellulose to absorb nitric acid that cannot be removed except by washing with water or by means of sulphuric acid insufficiently strong to dissolve the nitrocellulose (e.g. containing 50% of H_2SO_4) would seem to justify the supposition that nitrocotton is capable of forming complex compounds with nitric acid. There is however no other evidence in favour of this suggestion, although the formation of such complex compounds would appear possible.

NITRATION WITH MIXTURES OF NITRIC AND SULPHURIC ACIDS

The first attempts to nitrate cellulose by means of mixtures made up from nitric and sulphuric acids were made as early as by Vieille who in 1884 [1] also found that increasing the concentration of sulphuric acid in the mixture diminished the rate of the nitration reaction.

The rate of nitration of cellulose is dependent both on the rate of the chemical reaction of esterification itself, and on the rate of diffusion of the nitrating acid into the cellulose fibres. This is discussed later (p. 356).

The first extensive investigations into the relation between the nitrogen content of nitrocellulose and the composition of the mixed acid were carried out by Bruley [14]. They are summarized graphically in Fig. 119.

Lunge *et al.* [15] examined the effect of the composition of mixed acid, and the influence of the nitration temperature within the range from 0 to 80°C on the nitrogen content of nitrocellulose, the content of non-nitrated cellulose, the yield, the solubility of the products in ether–alcohol mixture and the viscosity of the acetone solution. Cotton linters were used. From these experiments it has been established that nitrocellulose containing more than 13.5% N is unstable and decomposed readily, as mentioned before.

Nitrocellulose containing 13.5% N can be obtained by nitrating with mixtures that are composed of sulphuric and nitric acid in various proportions, the water content being limited within 1 and 13%. Hence it can be concluded that in practice, the application of the most concentrated nitrating acids is not indispensable for producing nitrocellulose with the maximum nitrogen content (Table 71).

For mixed acids with a constant sulphuric to nitric acid ratio, the nitrogen content of the nitrocellulose falls as the proportion of water increases (Fig. 120).

After the water content in the mixed acid exceeds 13% the reaction proceeds more and more slowly. At the same time the solubility of the product increases up to a certain limit (Table 72).

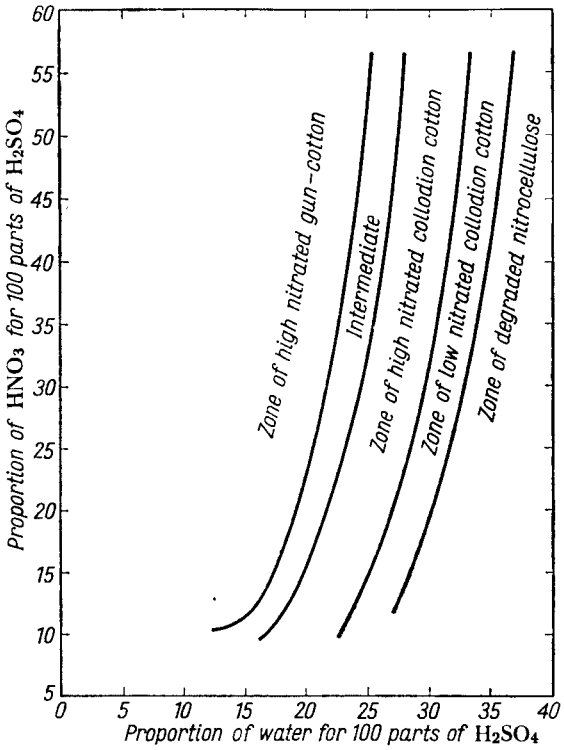

Proportion of HNO_3 for 100 parts of H_2SO_4
Proportion of water for 100 parts of H_2SO_4
Zone of high nitrated gun-cotton
Intermediate
Zone of high nitrated collodion cotton
Zone of low nitrated collodion cotton
Zone of degraded nitrocellulose

FIG. 119. Relation between the nitrogen content of nitrocellulose and composition of mixed acids, according to Bruley [14].

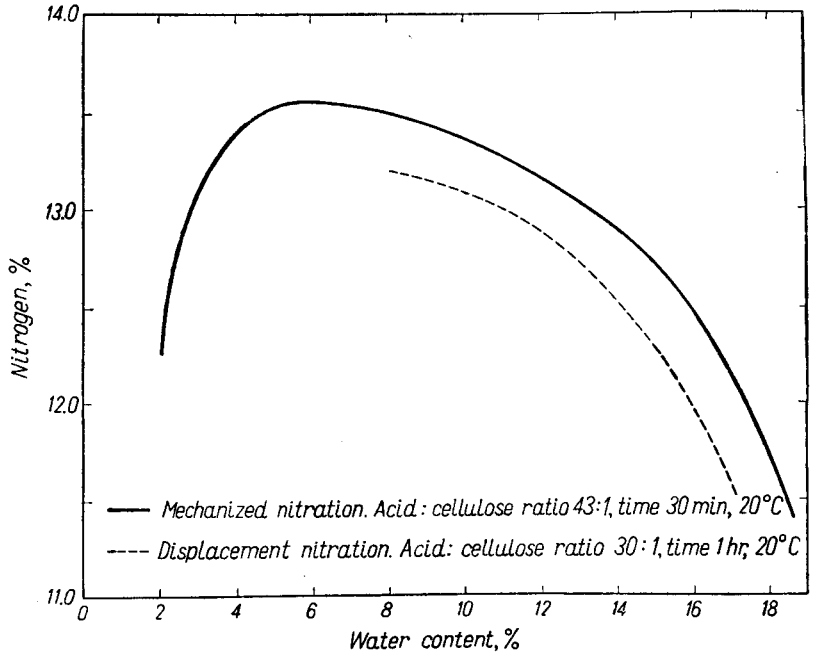

Nitrogen, %
Water content, %
Mechanized nitration. Acid : cellulose ratio 43:1, time 30 min, 20°C
Displacement nitration. Acid: cellulose ratio 30 : 1, time 1 hr, 20°C

FIG. 120. Change of nitrogen content in nitrocellulose as a function of water con-

TABLE 71

THE EFFECT OF NITRATING CELLULOSE WITH MIXED ACIDS OF DIFFERENT COMPOSITION (AFTER LUNGE [15])

No.	Composition of mixed acid, %			Nitrogen content of nitrocellulose %	Yield %
	H_2SO_4	HNO_3	H_2O		
1	60.00	27.43	12.57	13.62	173
2	62.10	25.79	12.11	13.75	174
3	62.95	24.95	12.10	13.83	175
4	63.72	25.31	10.97	13.75	175
5	64.56	24.65	10.79	13.71	175
6	68.02	25.28	5.70	13.76	—
7	64.55	26.55	8.88	13.72	173
8	63.35	25.31	11.34	13.92	173
9	75.33	22.80	1.87	13.53	176
10	74.16	22.12	3.72	13.51	175
11	72.97	21.63	5.40	13.57	—
12	69.90	20.45	9.65	13.64	177
13	68.31	20.49	11.20	13.61	176
14	67.43	19.37	13.20	13.25	172
15	67.32	32.53	0.15	13.62	176
16	65.41	31.34	3.25	13.57	175
17	63.75	30.80	5.45	13.63	176
18	60.68	29.31	10.01	13.68	176

At a water percentage of 25–27%, hydrocellulose and oxycellulose are formed to an extent large enough to bring about a decrease in yield, and to diminish the nitrogen value of the product below the limit required for commercial application.

Numerous investigators have drawn attention to the above mentioned fact that an anhydrous mixture produces nitrocellulose of a lower nitrogen content than a mixed acid slightly diluted with water. Rassow and Bongé [16] attained the highest nitrogen content of nitrocellulose by using a nitrating mixture containing 9–10% of water, and further reduction in the water content did not result in any increase in the nitrogen content of the nitrocellulose, as the reaction rate is slowed down. Thus an anhydrous mixture containing sulphuric and nitric acid in a 1:1 ratio results in a nitrogen content of 13.2–13.5% only after an interval of 12 hr, whereas adding 10% of H_2O to the same mixed acid makes it possible to shorten the time of nitration to only 45–60 min.

It has been confirmed by Schiemann and Kühne [17] that increasing the water content in the nitrating acid favours nitration. They reported that an almost anhydrous mixture, e.g. composed of 22.6% HNO_3, 76.6% H_2SO_4, 0.8% H_2O, gave a product of 12.9% N content, whereas increasing the proportion of water in this acid to 9.5% caused the nitrogen content to rise to 13.5%.

The origin of this phenomenon has not yet been made clear. Anhydrous acids seem likely to cause too rapid swelling on the surface of the cellulose fibres, so that the nitrating acid penetrates only with difficulty into the fibres.

Schiemann and Kühne also stated that changes in the water content of the mixed acid, maintained within the limits from 3.5 to 13.5%, do not, in fact, cause appreciable variations in the nitrogen content of nitrocellulose.

Lunge *et al.* [15] has examined the influence of the H_2SO_4:HNO_3 ratio on the rate of reaction, confirming the earlier observations of Vieille that increasing the amount of sulphuric acid decreases the rate of the chemical reaction. Thus the maximum degree of nitration is reached:

for a ratio of H_2SO_4:$HNO_3 = 1$ after 0.5 hr
H_2SO_4:$HNO_3 = 3$ after 3 hr
H_2SO_4:$HNO_3 = 8$ after 30 days

The highest nitrogen content is achieved by keeping the proportion of H_2SO_4:HNO_3 within the limits $\frac{1}{4}$–$\frac{3}{4}$.

Further increase in the value of the H_2SO_4:HNO_3 ratio reduces the nitrogen percentage of the nitrocellulose until at H_2SO_4:$HNO_3 = 8$, a considerable part of the cellulose remains un-nitrated. (Table 73).

TABLE 72 (LUNGE [15])

SOLUBILITY OF NITROCELLULOSE AS A FUNCTION OF COMPOSITION OF MIXED ACID AND OF NITROGEN CONTENT

Composition of the mixed acid, %			Nitrogen content %	Solubility in ether–alcohol %	Yield %
H_2SO_4	HNO_3	H_2O			
45.31	49.07	5.62	13.65	1.50	177.5
42.61	46.01	11.38	13.21	5.40	176.2
41.03	44.45	14.52	12.76	22.00	—
40.66	43.85	15.49	12.58	60.00	167.0
40.14	43.25	16.61	12.31	99.14	159.0
39.45	42.73	17.82	12.05	99.84	153.0
38.95	42.15	18.90	11.59	100.02	156.5
38.43	41.31	20.26	10.93	99.82	144.2
37.20	40.30	22.50	9.76	74.22	146.0
33.72	39.78	23.50	9.31	1.15	138.9
35.87	38.83	25.30	8.40	0.61	131.2
34.41	37.17	28.42	6.50	1.73	—

The problem of the rate of nitration of cellulose is discussed in a more detailed way in a special section — p. 355.

It should be borne in mind that laboratory experiments on the nitration of cellulose on a gramme scale usually using a large excess of acid, do not portray plant conditions in an exact manner. Under laboratory conditions a two hours' nitra-

TABLE 73

THE EFFECT OF $HNO_3:H_2SO_4$ RATIO (LUNGE [15])

$HNO_3:H_2SO_4$ ratio	After 1/2 hr		After 24 hr		After 15 days
	nitrogen content %	yield %	nitrogen content %	yield %	
1:1	12.58	162.75			
1:2	13.25	174.14			
1:3	12.72	166.14	13.40	176.44	
1:5	8.14	130.88	13.10	166.6	12.74% N
			After 3 days		After 30 days
1:8	24.44% unnitrated cellulose		10.86	151.6	11.70% N, 152% of yield, 4.48% unnitrated cellulose

tion is frequently carried out, whilst in commercial manufacture, the nitration time is considerably shorter. It might therefore be concluded that commercial techniques would produce a lower nitrogen content than reported for laboratory conditions. On the other hand industrial equipment permits a more effective stirring so as to obtain more uniform product, thus compensating for the short time of reaction.

When nitrating to a nitrogen content of 12% and more the nitration rate is higher, hence no significant divergence exists between nitration on the industrial scale and laboratory experiments.

Increase in the proportion of sulphuric acid in the mixture tends to reduce the chemical stability of the product, probably in consequence of the formation of unstable sulphuric esters of cellulose.

On varying the temperature of nitration from 0 to 80°C, Lunge observed that:

(1) the reaction rate increases appreciably with temperature increase;

(2) at a temperature above 40°C the nitrogen content of the nitrocellulose is decreased, remaining unchanged at temperatures between 60 and 80°C;

(3) elevation of the temperature causes a decrease in yield due to decomposition of the product;

(4) at a higher temperature, the solubility increases and the viscosity of the solutions falls lower and lower.

The first effort to formulate a theory explaining the nitration of nitrocellulose is to be found in a paper by Sapozhnikov [18]. This author paid special attention to the role of sulphuric acid in the nitration process. Sapozhnikov's theory has already been outlined (Vol. I, p. 9) so only certain assumptions he made as the basis for his speculation will be mentioned here.

Sulphuric acid acts as a dehydrating agent in the mixed acid. In this way a hydrate,

$H_2SO_4 \cdot H_2O$, is produced, accompanied by higher hydrated compounds defined by the formula $H_2SO_4 \cdot xH_2O$. Likewise nitric acid is capable of forming hydrates. Thus in the nitrating mixture an equilibrium corresponding to the eqn. (1) is postulated:

$$HNO_3 \cdot nH_2O + xH_2SO_4 \rightleftarrows HNO_3 + (n-x)H_2SO_4 \cdot H_2O \quad (1)$$

As the proportion of sulphuric acid in the mixture increases nitric acid loses water, because the affinity of H_2SO_4 for water is greater than that of HNO_3.

When the mole quantity of sulphuric acid balances the number of moles of water, i.e. when $n = x$, nitric acid loses all its water. Equation (1) is then converted to the form (2):

$$HNO_3 \cdot nH_2O + nH_2SO_4 \rightleftarrows HNO_3 + nH_2SO_4 \cdot H_2O \quad (2)$$

According to Sapozhnikov, the esterification proceeds most intensively in the presence of anhydrous nitric acid HNO_3, as in eqn. (2). In the presence of smaller amounts of sulphuric acid, nitric acid hydrates are formed; in practice they are not capable of esterifying cellulose.

Research on the nitric acid vapour pressure in the ternary system

$$H_2SO_4\text{–}HNO_3\text{–}H_2O$$

allowed Sapozhnikov suggest a hypothesis explaining the relationship existing between the HNO_3 vapour pressure and the form in which nitric acid is present in the nitrating mixture. Thus a maximum vapour pressure is correlated with anhydrous nitric acid, a lower pressure being shown by nitric acid in the form of the hydrate, $HNO_3 \cdot H_2O$, while an even lower value is shown by the hydrate $HNO_3 \cdot 3H_2O$.

On expressing the relationship between the nitric acid vapour pressure and the composition of the mixed acid, and on its capacity to nitrating cellulose, by means of graphs, Sapozhnikov saw that the curves showing the nitric acid vapour pressure and of those indicating the degree of cellulose nitration were very similar in appearance. He therefore deduced that the nitrating effectiveness of mixed acids was dependent on the nitric acid vapour pressures of the mixture (Vol. I., Fig. 3). Figures 121 and 122 give the nitration and HNO_3 partial pressure curves for nitrating mixtures in weight %.

As mentioned in Vol. I, Sapozhnikov's theory was abandoned for some time, but latterly it has been revived, mainly due to work byVandoni [19] and Miles [8] — see Vol. I.

From a study of the vapour pressures of the mixed acids, Miles has concluded that the highest nitrogen content is to be achieved by nitrating with a mixed acid consisting of:

HNO_3	24.3%
H_2SO_4	65.8%
H_2O	9.9%

This is closely in line with experimental data published by Lunge, quoted in

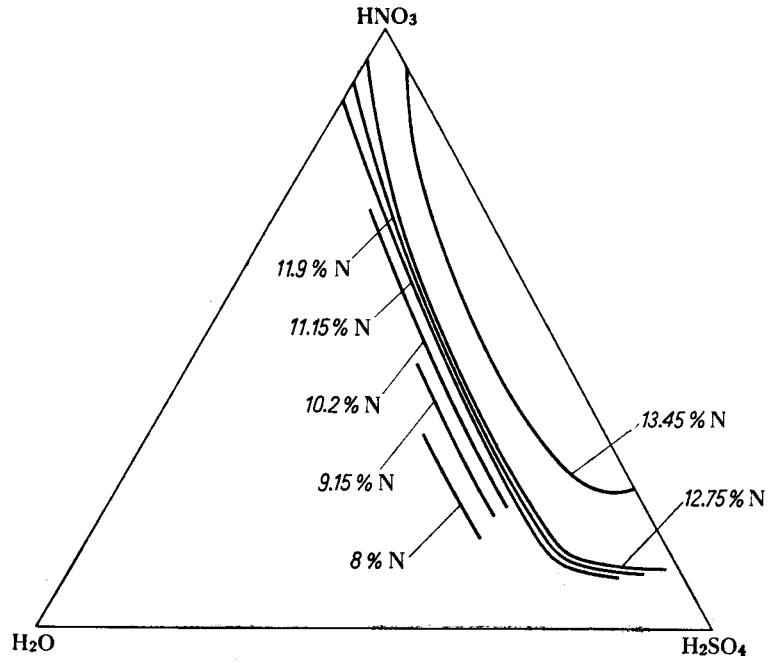


FIG. 121. Nitration of cellulose. A modified Sapozhnikov diagram with curves of equal nitrogen content in nitrocellulose. Composition of acid mixtures in weight %.

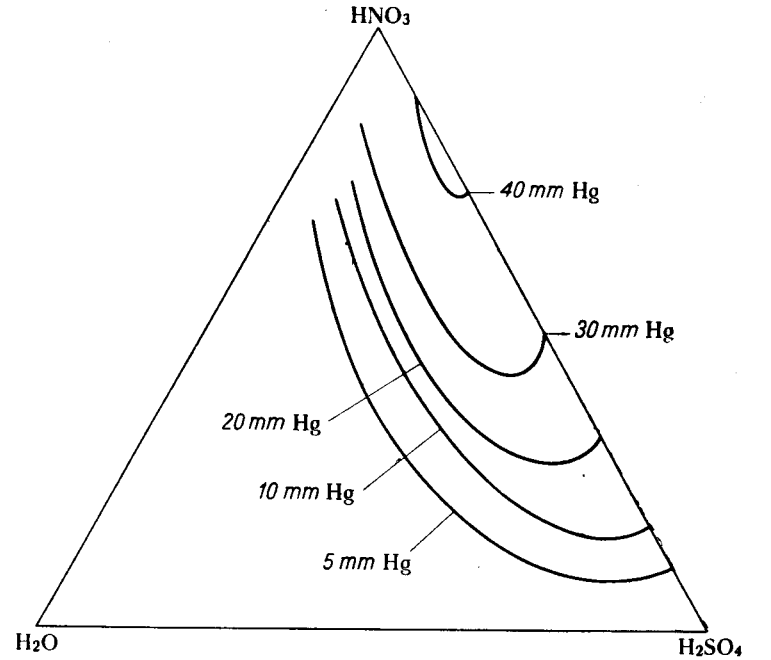


FIG. 122. Isobars of HNO_3 vapour pressure in nitrating mixtures. A modified Sapozhnikov diagram. Composition of acid mixtures in weight %.

Table 63 of this volume, which show that a nitrogen percentage of 13.92% may be attained, by using an acid composed of:

HNO_3	25.3%
H_2SO_4	63.4%
H_2O	11.3%

Miles and Milbourn [20] and Trogus [5] have revised Sapozhnikov's chart so as to indicate areas rich in water and most abundant in sulphuric acid, in which cellulose undergoes swelling at the time of nitration, the area richest in sulphuric acid where dissolution of cellulose prior to nitration proceeds and the zone defining mixtures being used in practice (Figs. 123 and 124).

Basing his view mainly on the theory of Hantzsch, that suggests that nitric acid at high concentrations exists in the form of the pseudo-acid $O_2N \cdot OH$, Farmer [21]

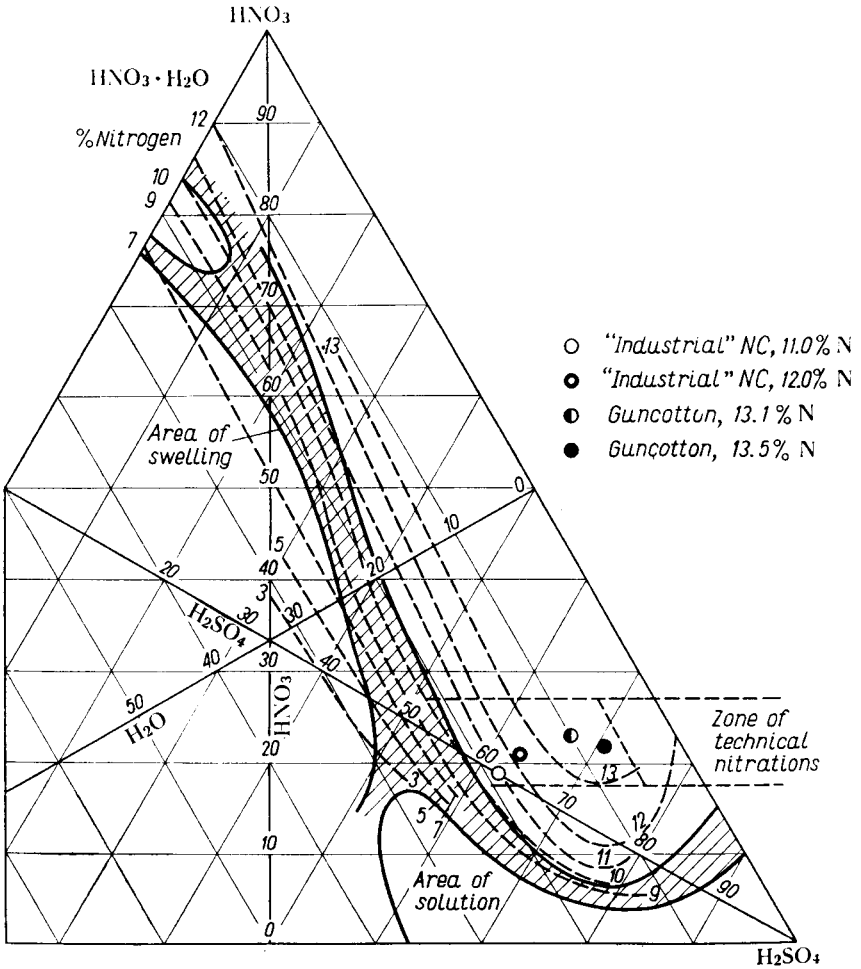


FIG. 123. Sapozhnikov diagram modified by Miles and Milbourn [20]. Composition of acid mixtures in weight %.

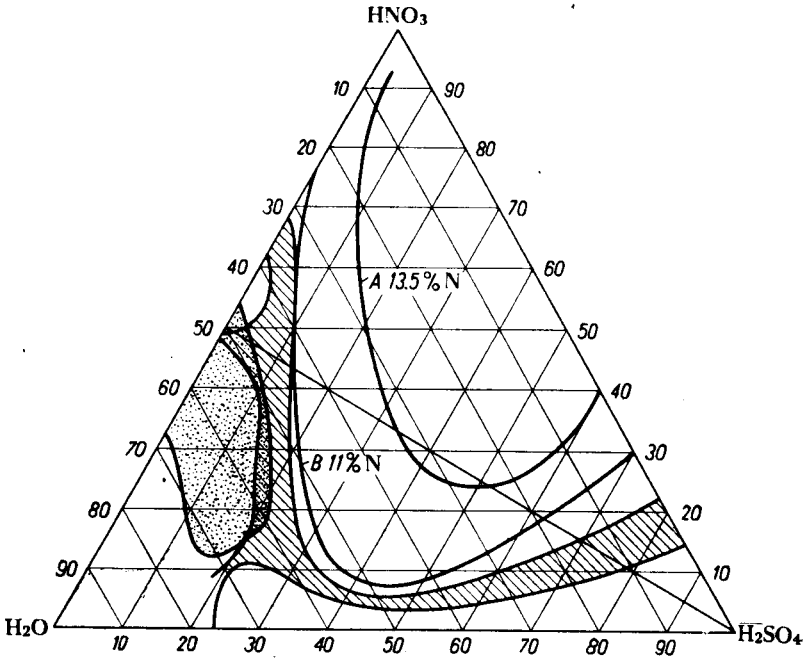


FIG. 124. Sapozhnikov diagram modified by Trogus [5]. Composition of acid mixtures in mole %.

suggested that nitric pseudo-acid is the active factor in the process of esterifying cellulose, similarly in the process of C-nitration. Sulphuric acid esterifies cellulose with difficulty, since it does not readily assume its pseudo-form. In a concentrated mixture of nitric and sulphuric acid, a nitronium sulphate is formed thus decreasing the concentration of the pseudo-acid form of nitric acid. In anhydrous nitric acid nitronium nitrate, which is also a salt inactive as an esterifying agent, should be present. Farmer thus explained the well-known observation that the esterifying capacity of a concentrated nitric acid and that of concentrated mixed acid is lower than that of acid containing a small proportion of water. The concentration of nitric pseudo-acid is highest in mixtures containing about 10% of water.

Berl *et al.* [22] established that the upper limit of cellulose nitration is reached when the composition of the nitrating mixed acid has the mole ratio

$$\frac{HNO_3}{H_2SO_4 \cdot H_2O} = \frac{1}{2}$$

Such a mixed acid corresponds with the following weight percentage of ingredients:

HNO_3	21.8%
H_2SO_4	66.0%
H_2O	12.2%

and is thus well in line with experimental values.

According to Chédin *et al.*, the higher the concentration of nitronium ions $NO_2^{\oplus}$ in the nitrating acid the more complete the nitration of nitrocellulose. Chédin [23] has produced a graph (Fig. 125) depicting the composition of mixed acids and their effect on cellulose. Thus, in the area *II*, rich in sulphuric acid but poor in nitric acid and water, a rather low concentration of $NO_2^{\oplus}$ is found, though

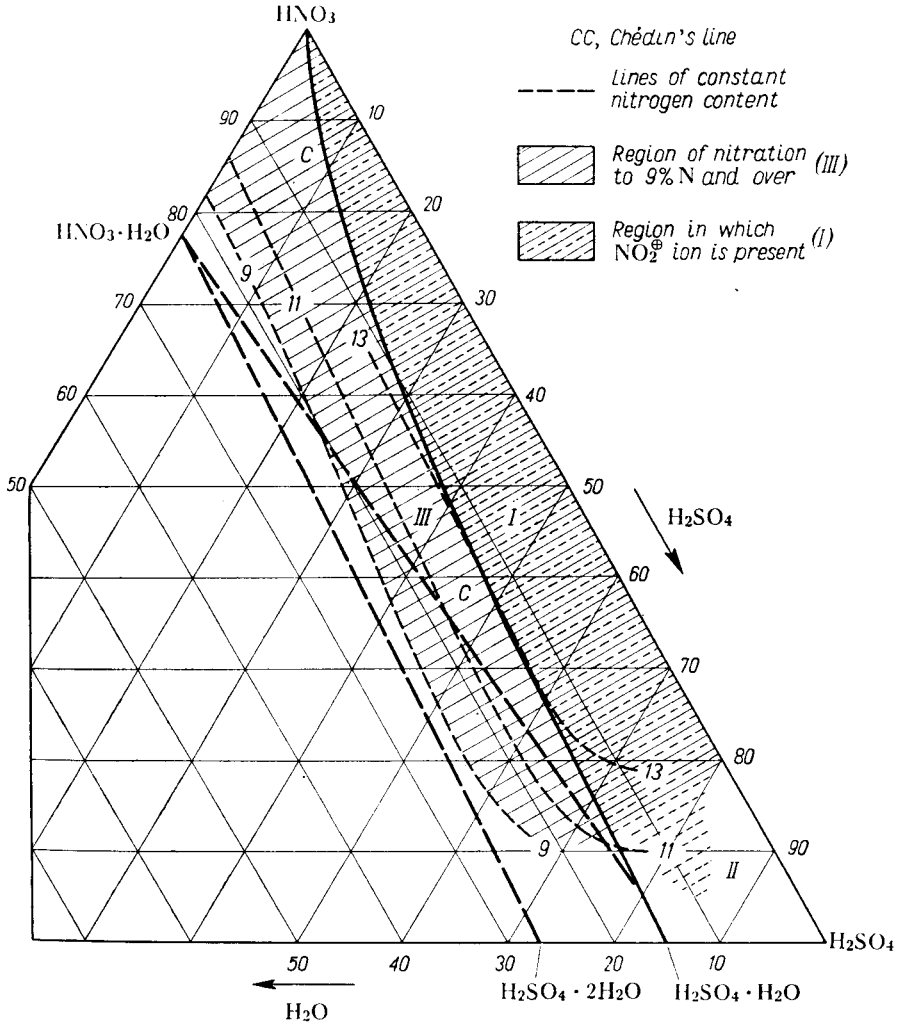


FIG. 125. Diagram of Chédin [23]: limits of compositions, nitrating cellulose, according to Miles [8].

almost the whole of the nitric acid is dissociated into $NO_2^{\oplus}$ and $OH^{\ominus}$ ions. This is why the degradation of cellulose predominates here, while nitration occurs only to an unimportant extent. Within the region *I*, cellulose is nitrated to a nitrogen value as high as 13.75% N. Nitric acid is only partially dissociated here, while sulphuric acid can be hydrated. In the area *III*, the $NO_2^{\oplus}$ ions are not detectable by spec-

trographic measurements. The nitrogen content of nitrocellulose is lower under these conditions. It falls considerably as the mixed acid is diluted with water.

The role of sulphuric acid during nitration is not limited to participation in the creation of the $NO_2^{\oplus}$ ions nor to binding water, however. Increase in the amount of sulphuric acid causes the ester produced, i.e. cellulose nitrate, to hydrolyse since the reaction is reversible.

The hydrolytic activity of sulphuric acid is one of reasons why efforts to obtain cellulose trinitrate by treatment with mixtures composed of nitric acid and sulphuric acid were a failure. The maximum percentage of nitrogen combined in ester form was not higher than 13.96%.

Berl and Klaye [24] pointed out the reversibility of the esterification reaction, and stated that the degree of cellulose nitration was dependent primarily on the final composition of the mixed acid.

Japanese authors [25, 26] were the first to formulate the nitration equilibrium in terms of the activities of nitric acid and water in the nitrating mixtures (see p. 357). It is self-evident that the final composition of the mixed acid differs from the initial one, as nitric acid is consumed and water is produced during the course of the reaction. Therefore the content of nitro groups in the nitrocellulose does not depend solely on the composition of the mixed acid, but also on the excess of acid, and thus it depends on the cellulose to acid ratio. If the excess of mixed acid is large enough, its dilution by water formed during nitration, and the consumption of nitric acid, is relatively unimportant. Hence the nitrogen content of nitrocellulose is higher.

If it is desired that the composition of the nitrating mixture should change as little as possible during the nitration, a large excess of acid must be used. In commercial practice a cellulose to acid ratio of 1:50 is usually used. This is 10–15 times as much acid as needed in relation to the amount of nitric acid calculated from theory.

To designate the change in composition of mixed acid brought about by nitration, Schiemann and Kühne [17] reported the data given in Table 74.

TABLE 74

CHANGE IN THE MIXED ACID RATIO AFTER NITRATION

Composition of the nitrating mixture, %			Composition of the spent acid, %			Cellulose to acid ratio	Nitrogen content of nitrocellulose, %
HNO_3	H_2SO_4	H_2O	HNO_3	H_2SO_4	H_2O		
24.78	70.82	5.40	20.69	71.29	8.02		
23.05	68.07	8.88	18.20	69.56	12.24	1:50	13.0–13.5
21.09	68.52	10.19	16.91	69.10	13.99		
22.65	76.50	0.85	21.80	76.71	1.49		
21.73	73.15	5.12	20.29	74.37	5.34	1:80	12.9–13.5
20.70	69.45	9.78	19.58	70.12	10.30		

Treating nitrocellulose with a mixed acid capable of producing cellulose nitrate with a lower nitrogen value results in a partial denitration of the cellulose. On the other hand nitrocellulose immersed in a mixture of concentrated acids undergoes further nitration. Berl *et al.* [24, 27] have reported unquestionable examples. For instance three samples of nitrocellulose of different nitrogen content: 10.9, 12.7, and 13.5% respectively, were drowned in two nitrating acids. After a sufficiently long time each of the three samples of nitrocellulose immersed in any one of the mixed acids showed the same percentage of nitrogen.

Cotton and guncotton No. 1 (high nitrated guncotton) were treated with a nitrating mixture consisting of

H_2SO_4	60.0%
HNO_3	22.5%
H_2O	17.5%

by Demougin and Bonnet [28]. In both instances, after specific times nitrocotton of the same nitrogen content was obtained, as shown in Table 75.

TABLE 75

CHANGING NITROGEN CONTENT (% N) IN SAMPLES OF COTTON IMMERSED IN MIXED ACID [28]

After the period of	15 min	1 hr	4 hr	24 hr	4 days	7 days	60 days
Cotton	11.62	11.81	12.84	12.32	12.41	12.62	12.65
Guncotton No. 1	13.33	13.23	13.09	12.99	12.94	12.87	12.66

Demougin and Bonnet reported that both these reactions occurred at the same rate in conc. acids, equilibrium being established after about fourteen days. With nitrating acids containing an exceptionally high percentage of water, i.e. 21.7% water in experiments of Miles and Milbourn [20], or 24.6% in the experiments of Berl and Hefter [27], the balance tends to establish itself very slowly, and considerably altered products are formed due to side reactions. Efforts to achieve an absolute equilibrium fail in such instances.

The results obtained by de Bruin and Witte [28a] make it clear that denitration of nitrocellulose with mixed acid may not reach completion even after one year (e.g. denitration of nitrocellulose of 13.95% N with mixed acid containing 21.9% HNO_3 and 16.9% H_2O which yields nitrocellulose of 12.4% N on nitration).

The authors also denitrated nitrocellulose with nitric acid, obtaining rather non-uniform products.

They pointed out that the rate of denitration is much lower than that of nitration. A theory recently advanced by Trommel [80] explained this in terms of the relative accessibility of the reacting groups in cellulose and nitrocellulose (see p. 239).

Fabel and Fritsche [29] have carried out experiments designed to re-nitrate and denitrate nitrocellulose, as follows. Cellulose was at first nitrated by immersion for 1 hr in one of a series of mixed acids: A, B, C, or D (see Table 76). In succession

TABLE 76

COMPOSITION OF MIXED ACIDS USED IN THE EXPERIMENTS OF FABEL AND FRITSCHE [29]

Composition, %	A	B	C	D
HNO_3	20.4	20.4	20.3	20.3
H_2SO_4	65.5	62.0	59.6	58.1
H_2O	14.1	17.6	20.1	21.6

each sample of nitrocellulose, except D, was divided into 4 parts, to be immersed in the other (or the same) nitrating acid, for 4 hr. Products of nitrogen content shown in Table 77 were obtained.

TABLE 77

Nitrating acid	First nitration % N	(% N) Re-nitration in the mixture			
		A	B	C	D
A	13.05	13.07	12.77	12.12	12.01
B	12.24	13.12	12.49	11.69	12.26
C	11.19	13.07	12.48	11.50	10.84
D	10.15	—	—	—	10.53

The figures indicate the result of the additional re-nitration and the effect of denitration, respectively.

Extensive research has been carried out by Wilson and Miles [10] on the denitration of nitrocellulose by the mixed acid. They investigated the influence of acids that varied in chemical composition within wide limits (the content of nitric acid varied from 10 to 70%). A couple of noteworthy rules were formulated. Thus, they found that the higher the proportion of nitric acid, the more rapid the rate of denitration. Sulphuric acid alone or a mixture containing a small amount of nitric acid, e.g. 6% of HNO_3 and 68% of H_2SO_4, has a very weak denitrating effect. The quickest denitration occurs in the presence of acids able to cause cellulose to swell, if such acids are used for the nitration. The higher the nitrogen content of the substance undergoing denitration, the more rapidly denitrating proceeds. Raising the temperature causes the rate of denitration to increase appreciably.

The following example is described by these authors: nitrocotton of 12.2% N was denitrated down to 10.7% N in the presence of acid of 69% HNO_3 and 19% H_2O at 20°C for 5 hr, whilst at 60°C, denitrating to 10.0% N was accomplished within 3 min.

The products obtained by denitrating to below 9.5% N are not completely soluble in acetone.

Craik [30] has determined the influence of temperature, and in consequence the effect of the denitration rate, on the solubility of nitrocellulose (Table 78).

TABLE 78

Denitration	% N		Denitrating acid		Temperature °C	Time hr	Solubility, %	
	Before	After	% HNO_3	% H_2O			Acetone	Alcohol–ether
Slow	13.43	12.78	41.3	20.3	20	72	100	2.3 (before the reaction)
							100	99.5 (after the reaction)
Rapid	13.10	9.5	37.2	28.4	55	3/4	100	5.3 (before the reaction)
							1.5	0.9 (after the reaction)
Rapid	12.55	10.8	38.8	25.3	35	1/2	100	100 (before the reaction)
							100	33.5 (after the reaction)

While regarding the formation of the O-nitro derivative of cellulose as an effective resultant from the nitration and denitration processes, the following picture of the course of reaction leading to the formation of nitrocellulose should be kept in mind.

(1) A portion of the cellulose brought into contact with fresh mixed acid is nitrated to a high nitrogen content. The acid is diluted by water produced during the reaction.

(2) Another portion of cellulose not nitrated so as to form a higher nitrated substance, reacts to give a product containing a lower percentage of nitrogen since the mixed acid has been diluted during stage (1). Gradually further dilution of the acid takes place.

(3) Higher nitrated fractions suffer hydrolysis due to the presence of the more dilute acid.

The process (3) may be slow, hence under industrial conditions it may be broken off before the equilibrium is established. This means that the chemical reaction (3) is not completed. As a final product, a not very homogeneous nitrocotton is obtained. The higher the nitrating temperature, the more rapid the denitration process, the sooner the reaction balance is established, and hence the more uniform the product.

The following formulae, intended for calculating the ratio of components in the mixed acid after equilibrium is established, have been published by Miles [8]:

$$D_n = \frac{100-n}{31.13\frac{R}{N} - R - 1} \qquad D_w = \frac{40+w}{31.13\frac{R}{N} - R - 1},$$

where: N nitrogen content of nitrocellulose as % N,
n the nitric acid concentration in the mixed acid as % HNO_3,
w the water concentration in the mixed acid as % H_2O,
R the weight ratio of mixed acid to cellulose,
D_n the difference in the nitric acid percentage of the mixed acid before and after the nitration,
D_w the difference in the water percentage in the mixed acid before and after the nitration.

Taking into consideration the results of experiments reported by different authors, Berl, Andress and E. Escales [31] have constructed a chart resembling Sapozhnikov's graph, to depict the relationship between the nitrogen content of nitrocellulose and the ratio of spent acid (Fig. 126). In principle the shape of the curves does not differ from those outlined in Sapozhnikov's work and a resemblance exists between those curves and the curves of nitronium ions ($NO_2^{\oplus}$) concentration (Fig. 125).

The same observations apply to the graph of nitrating starch discussed in one of the following chapters, with the exception that the solubility of nitrostarch in nitrating mixtures is, however, a major factor. Thus mixed acids of poor sulphuric acid percentage dissolve nitrostarch, and esterification in such homogeneous systems proceeds more readily.

NITRATION WITH MIXTURES OF NITRIC AND PHOSPHORIC ACIDS

The attempt to substitute phosphoric acid for sulphuric acid was first made by Hoitsema [32] and was also investigated independently at the same time by Lunge and Weintraub [15]. Work in this field has been revived by Krauz and Blechta [33], Berl and Rűff [34], Bouchonnet, Trombe, Petitpas [35], Staudinger and Mohr [35a] and Wannow [36].

Hoitsema obtained a nitrogen content as high as 14.0% N. The works of Berl and Rűff showed that the highest rate of nitration was obtained with mixtures having a phosphoric acid to nitric acid ratio varying within the limits of 3:1 and 1:1. By using these nitrating acids, Berl and Rűff obtained nitrocellulose containing 13.5% N within 1½ min.

Increasing the content of phosphoric acid above 75% of the total mixture is accompanied by a significant reduction in the reaction rate. The nitrogen content of a product prepared by nitrating with mixtures of HNO_3 and H_3PO_4 is higher

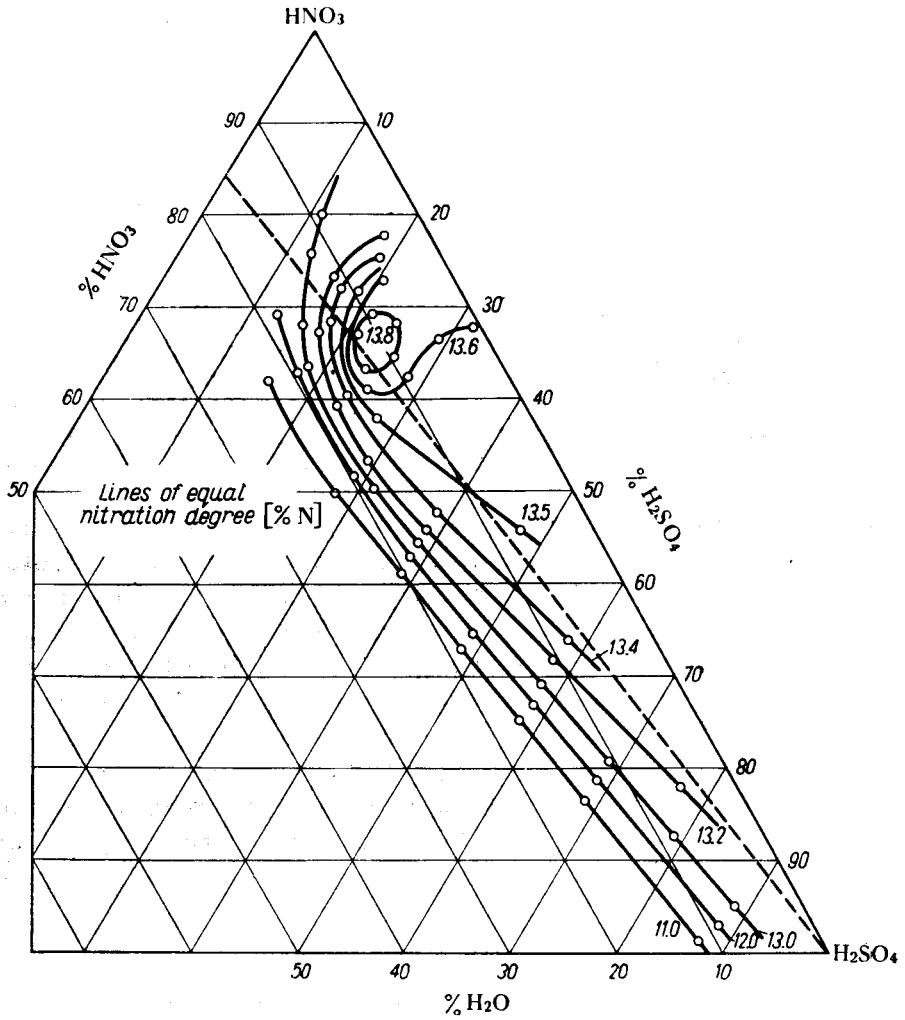


FIG. 126. Nitration of cellulose as a function of the terminal composition of nitrating mixtures (Berl, Andress and E. Escales [31]).

than when mixed acid of HNO_3 and H_2SO_4 are used. This is due to the fact that phosphoric acid does not act as a hydrolysing agent on the cellulose nitrate produced.

The recent systematic investigations carried out by Newman *et al.* [37] were devoted to the viscosity, sedimentation, diffusion and osmotic pressure of nitrocelluloses prepared by nitrating non-purified cotton, purified cotton, and viscose fibres with mixed acid containing phosphoric acid and phosphoric anhydride.

The nitrogen value obtained was reported to be 13.34–13.61% N.

Wannow [36] has stated that the nitration of cellulose by means of mixed nitric and phosphoric acid does not reduce the degree of polymerization of the nitrated substance. The stability of nitrocellulose obtained by treatment with H_3PO_4 and HNO_3 is

excellent, as there are no sulphuric esters tending to decompose. Phosphoric acid cellulose esters, if produced, are not characterized by poor stability.

According to Lenze and Rubens [38], the application of concentrated nitric acid with phosphoric anhydride P_2O_5 makes it possible to attain a nitrogen content close to 14.1%, i.e. approximately that of the pure trinitrate.

Several investigators (Berl and Rűff [34], Staudinger and Mohr [35a], Davidson [39], Wannow [36]) have stated that nitrating cellulose by means of a mixture consisting of nitric acid and phosphoric acid gave an appreciably less de-polymerized, although more swollen product than one resulting from the usual nitration by a mixed acid made of nitric and sulphuric acid. For this reason Davidson has recommended nitrating cellulose with mixture of nitric acid and phosphoric acid in order to determine the molecular weight of the nitrocellulose and hence to estimate the molecular weight and the degree of polymerization of the original, untreated cellulose. Davidson reported the following preparative method as suitable for this purpose: one part by weight of cellulose is stirred into 100 parts by weight of a mixture prepared from:

HNO_3	48% by weight
H_3PO_4	50% by weight
P_2O_5	2% by weight

cooled —10°C. After the cellulose has been introduced a temperature of 0°C is maintained for 4–6 hr. The product is filtered off in a suction funnel, and subsequently washed with a mixture of acetic acid and water in a 1:1 volume ratio. During this operation the temperature must be kept at —10°C. The product is rinsed with distilled water until its reaction is neutral. Then it is allowed to stand overnight in a large amount of distilled water, after which it is subjected to a threefold boiling, each lasting 3 hr.

Using the ultracentrifuge sedimenting method, Gralen and Svedberg [40] have determined the molecular weight of nitrocellulose prepared from various types of cellulose. The nitration was carried out at 0°C by means of a mixture composed of 40% of nitric acid, 40% of phosphoric acid, and 20% of phosphorus pentoxide. The results are collected in Table 79.

It follows from these values that the degree of degradation is not inconsiderable, since it corresponds with a two- to three-fold reduction in molecular weight, in spite of the conditions of nitration. The results clearly disagree with those obtained by Staudinger and Mohr [35a] and reported earlier on p. 246.

It has been stated on the basis of trials carried out in the factory at Angoulême, France [41], that the method of nitrating with a mixture composed of nitric and phosphoric acid can be successfully applied commercially for manufacturing high nitrated guncotton (CP_1) containing 13.7% of nitrogen. On the other hand it is less suitable for the production of low nitrated guncotton with a nitrogen percentage of about 12%, since it yields a non homogeneous product.

Nitration by means of nitric and phosphoric acid appears to have prospects of being adopted industrially. However, the use of mixtures containing phosphoric acid involves great technical difficulties, as for instance, the greater tendency of

TABLE 79

Type of cellulose	Cellulose		Nitrocellulose	
	$M \times 10^{-6}$	Polymerization degree	$M \times 10^{-6}$	Polymerization degree
Unbleached cotton Linters	1.75	10,800	0.78	2700
Bleached cotton Linters	0.41	3000	0.40	1360
Sulphite wood pulp	0.46	2900	0.43	1470
Sulphate wood pulp	0.40	2500	0.42	1450

phosphoric acid, as compared with sulphuric acid, to corrode iron and steel. Besides, the recovery of the spent acid is considerably more complicated, since extraordinarily high temperatures for distillation are necessary.

NITRATION WITH MIXTURES OF NITRIC AND ACETIC ACIDS (OR ACETIC ANHYDRIDE)

Acetic acid, or acetic anhydride can be used in the manufacture of nitrocellulose as dehydrating agents. Berl and Smith [42] showed that increasing the proportion of acetic acid mixed with 88% nitric acid favours the nitrating capacity of the mixed acid, since they obtained products containing 13.7–14.0% of nitrogen.

Trogus [43] used the Berl and Smith method to prepare nitrocellulose for X-ray investigations, because it showed the least swelling. Recently Harland [44] has suggested using a mixed acid composed of nitric acid, acetic acid and acetic anhydride when preparing nitrocellulose for the determination of the molecular weight and the degree of polymerization by viscometry. This proposal followed from his observation that cellulose undergoes virtually no de-polymerization when nitrated with a mixed acid of this kind.

Darzens [45] has claimed that nitrating cellulose in a homogeneous mixture of nitric acid, acetic anhydride and chloroform makes it possible to obtain a product containing as much as 13.7% of nitrogen.

It has been established (Bouchonnet, Trombe and Petitpas [35]) that cellulose trinitrate with 14.14% N can be obtained as result of nitrating linters with a mixture composed of 50% of nitric acid, 25% of acetic acid and 25% of acetic anhydride for 5 hr at 15°C. The product was stabilized by alcohol extraction.

NITRATION IN MIXTURES AND SOLUTIONS INCLUDING INACTIVE SUBSTANCES

The earliest attempt to nitrate cellulose in mixtures comprising inactive substances was made by Rogovin and Paradnia [46]. The experiments were aimed at investigating the possibility of replacing the large excess of sulphuric acid which does

not take part in the chemical reaction, and exerts an adverse influence on nitrocellulose, for in the presence of a relatively high percentage of water in the mixed acid, it favours side reactions, and oxidizes and hydrolyses the nitrocellulose.

Rogovin and Paradnia substituted carbon tetrachloride or pentane for a part of the mixed acid, and obtained nitrocellulose with different nitrogen values. With a low water content, and a ratio HNO_3:H_2SO_4 of 3:1, and by varying the proportion of the inert substance for 75–87%, they obtained nitrocellulose of different nitrogen contents.

Thus for instance, nitration in the mixture composed of

HNO_3	18%
H_2SO_4	5%
NO_2	2%
CCl_4	75%

to which an emulsifying agent (naphthalenesulphonic acids) had been added, gave nitrocellulose containing 11.7% N. An increase of the carbon tetrachloride percentage to 87.5% caused the nitrogen value to decrease to 10.6%.

Kenyon *et al.* [47] published a graph (Fig. 127) showing the effect of the nitric

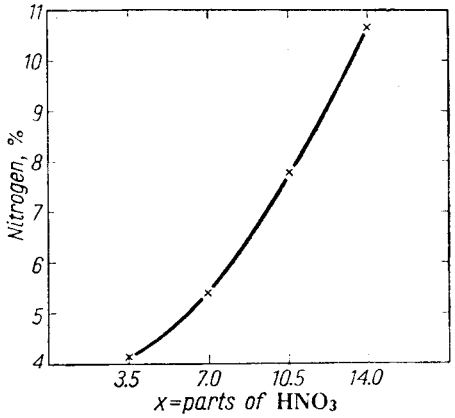


FIG. 127. Nitrogen content in nitrocellulose as a function of HNO_3 concentration in carbon tetrachloride. Ratio of reactants 5:1:x (cellulose : CCl_4:HNO_3) (Kenyon *et al.* [47]).

acid concentration in the carbon tetrachloride on the nitrogen percentage of the nitrocellulose produced. The conditions of experiment were as follows: for 5 parts of cellulose, 120 parts of carbon tetrachloride mixed with varying amount of anhydrous nitric acid were used to carry out the chemical reaction for 1 hr.

In addition, there are a few references in the literature describing experiments to nitrate cellulose in media comprising solvents resistant to nitration such as chloroform and other chlorinated hydrocarbons.

Thus, Bouchonnet [48] nitrated cellulose in a solution of nitrogen pentoxide in carbon tetrachloride, to obtain a stable cellulose trinitrate of 14.1% N. Similar

products, i.e. with a nitrogen percentage of 13.9–14.1%, have been obtained by this worker, using other solvents, namely chloroform and dichlorodiethyl ether. Ethyl ether includes a characteristically "basic" oxygen atom that forms addition compounds with nitric acid, hence it hinders for the nitration process. Dichlorodiethyl ether, on the other hand, does not behave in this way so that nitration to trinitrate is possible.

In the thirties a new commercial method of nitrating cellulose was invented in Germany by Thinius and Weihe [49]. It consists in acting upon cellulose with anhydrous nitric acid dissolved in organic solvents that do not enter into reaction with this acid, and which do not dissolve nitrocellulose. After being separated, the product is stabilized by ordinary methods. Nitrocellulose produced in this way is characterized by high purity and long-lasting stability.

Rogovin and his colleagues [50] nitrated cellulose by means of nitric acid dissolved in methyl nitrate. Nitrocellulose containing 13.7–14.0% N was obtained with the help of 2 parts of anhydrous acid added to 3 parts of methyl nitrate, allowed to react with the raw material for a period 2 hr at 35°C. Using nitric acid 95% a product containing 10.1% N was obtained under the same conditions. A large proportion of the nitrocellulose containing more than 10% N was dissolved in the nitrating solution. The product can be separated by precipitation with water.

NITRATION WITH NITRIC ACID IN THE PRESENCE OF INORGANIC SALTS

A series of investigations has been devoted to the problem of nitrating cellulose with nitric acid mixed with inorganic salts. Thus for example, Bouchonnet, Trombe and Petitpas [51] have established that the nitration of cellulose by means of anhydrous nitric acid containing an admixture of different salts may yield nitrocellulose with a high nitrogen content shown in Table 80.

TABLE 80

THE EFFECT OF NITRATING CELLULOSE WITH 100% NITRIC ACID IN THE PRESENCE OF DIFFERENT SALTS [51]

Salt	Content of salt in nitric acid, %	Content of nitrogen in nitrocellulose, %
No salt	–	13.3
NH_4NO_3	12	13.87
K_2SO_4	13–15	13.87
KH_2PO_4	20	13.87
$(NH_4)_2SO_4$	10	13.81
KNO_3	30	13.81
$NH_4H_2PO_4$	12–15	13.91

Hence salts exert a characteristic effect that brings about an increase in the nitrogen content of the nitrocellulose.

When 97% nitric acid was used with an addition of 14–16% potassium nitrate nitrocellulose containing 13.37% N was produced.

T. Urbański and Szypowski [52] obtained slightly different results on nitrating linters (98.6% of α-cellulose) by means of fuming nitric acid 98.6% HNO_3, with admixtures of different salts, as shown in Table 81.

TABLE 81

THE EFFECT OF NITRATING CELLULOSE WITH 98.6% NITRIC ACID IN THE PRESENCE OF DIFFERENT SALTS [52]

Salt	Content of salt in nitric acid, %	Content of nitrogen in nitrocellulose, %
No salt	–	12.85–12.90
$NaNO_3$	5	13.35
	9	13.26
KNO_3	5	13.20
	10	13.25
	20	13.07
	30	12.70
NH_4NO_3	5	13.32
	10	13.18
	20	13.02
	35	10.80
$Ca(NO_3)_2$	5	13.20
$Mg(NO_3)_2$	5	13.50
Na_2SO_4	4	13.52
$NaHSO_4$	5	13.42

The maximum nitrogen content of nitrocellulose was reached in these experiments when a 5% solutions of sodium, potassium or ammonium nitrate in nitric acid were used. The highest nitrogen percentage, i.e. 13.5%, was attained when using anhydrous salts that readily form hydrates, namely magnesium nitrate, $Mg(NO_3)_2$, and sodium sulphate, Na_2SO_4.

NITRATION WITH NITROGEN OXIDES

The investigations of Lunge and Bebie [15] made it clear that dinitrogen tetroxide, present in the mixed acid up to 6%, had no adverse influence on the degree of esterification of cellulose. It is known that dinitrogen tetroxide reacts in the presence of sulphuric acid so as to form one molecule of HNO_3 from one molecule of dinitrogen tetroxide:

$$N_2O_4 + H_2SO_4 \longrightarrow HOSO_2ONO + HNO_3 \qquad (3)$$

Pinck [53] examined the nitrating activity of such a mixture, and obtained nitrocellulose with various nitrogen contents, rising to 13.36%, when nitric acid containing 15% N_2O_4 mixed with 95% sulphuric acid was used.

An important contribution was made by Rogovin and Tikhonov [54] who followed the nitration of cellulose by means of nitric acid including different quantities of nitrogen trioxide N_2O_3, dinitrogen tetroxide N_2O_4, or nitric anhydride N_2O_5. In every instance the degree of nitration was higher than could be achieved by nitration with nitric acid alone. The presence of nitrogen trioxide and tetroxide causes cellulose to de-polymerize during nitration. Because of this, the viscosity of nitrocellulose prepared in this way is lower than that made by esterification in the presence of nitrogen pentoxide. Likewise the stability of nitrocotton produced in the presence of N_2O_3 and N_2O_4 is lower than that of nitrocellulose yielded in effect of nitration accompanied by N_2O_5.

Nitration by means of 96% nitric acid enriched with 4% nitrogen pentoxide results in a nitrocellulose containing 13.7% N of good stability, while nitration with 96% nitric acid alone yields a product with 13.0% N. This has been confirmed by many research workers, using N_2O_5 in various ways for nitration. Thus Hoitsema [32] obtained nitrocellulose containing 14% N, while Berl and Klaye [24] produced one with 13.86% N. Lenze and Rubens [38], using nitrogen pentoxide dissolved in nitromethane, obtained nitrocellulose of 14% N. Dalmon, Chédin and Brissaud [55] showed that a solution of N_2O_5 in carbon tetrachloride produced nitrocellulose which contained 14% N.

T. Urbański and Janiszewski [56] have confirmed the results of their predecessors, using nitrogen pentoxide plus a small amount of nitric acid, intended for preparing a liquid nitrating solution. Within 40 min at 20°C or after 35 min at 45°C, a product containing 14.0% N was reached. This kind of nitrocellulose is characterized by its high stability.

Rogovin and Tikhonov [54] reported cellulose nitrated in solutions of nitrogen trioxide N_2O_3 in nitric acid formed the nitrates described in Table 82.

TABLE 82

THE EFFECT OF NITRATING CELLULOSE WITH SOLUTIONS OF N_2O_3 IN NITRIC ACID [54]

Concentration of N_2O_3 %	Nitrogen content of nitrocellulose %	Viscosity of a 2% acetone solution	Stability at 110°C hr
—	13.03–13.06	312	4.5
2	13.3 –13.4	—	4
3	13.4 –13.5	159	4
4	13.4 –13.5	96	1.75
10	9.6 – 9.4	12	1.33

On carrying out the nitration by means of nitric acid plus N_2O_4, these investigators observed results intermediate between the action of N_2O_3 and N_2O_5 (Table 83).

Examining the action of dinitrogen tetroxide alone in liquid or gaseous form, or dissolved in nitric acid, Shorygin and Khait [57] found that N_2O_4

TABLE 83

THE EFFECT OF NITRATING CELLULOSE WITH SOLUTIONS OF N_2O_4 IN NITRIC ACID [54]

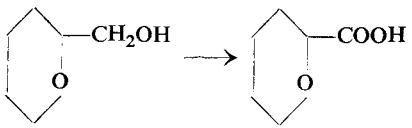
Concentration of N_2O_4 %	Nitrogen content of nitrocellulose %	Viscosity of a 2% solution in acetone	Stability min
—	13.0	312	240
2	13.35	150	—
4	13.65	175	150
10	13.65	193	90

caused considerable degradation of the cellulose, but no nitration. Only oxidation products of acid character soluble in sodium carbonate solution are formed under these conditions. Nitric acid with dinitrogen tetroxide dissolved in it gives nitrocellulose of a higher nitrogen content, if the content of N_2O_4 is kept within the limit of 20–30%. In the presence of a larger percentage of N_2O_4 the degree of nitration falls.

Cellulose regenerated by treatment with ammonium sulphide suffered extensive degradation on nitration in the presence of dinitrogen tetroxide.

Shorygin and Khait [57] first drew attention to the fact that cellulose brought into contact with nitrogen dioxide is converted into a substance totally soluble in alkali solution. This reaction was then investigated in more detail by Kenyon *et al.* [58] as well as by Rogovin *et al.* [59].

It has been made clear that the primary hydroxylic groups undergo oxidation, and as a result macromolecules comprising units of glucuronic acid are formed:



It is possible to oxidize all the CH_2OH groups to carboxylic groups, if the conditions of reaction are sufficiently severe, when the content of COOH may reach 25%. The product obtained in this way is a polyanhydroglucuronic acid, known as carboxycellulose or celluronic acid. When half the CH_2OH groups present in the cellulose are oxidized, a product with a 13% COOH content is obtained, soluble in dilute solutions of caustic soda, ammonia and sodium carbonate. Celluronic acid can form esters with nitric acid. The properties of these esters will be discussed later.

According to the more recent investigations of Nabar and Padmandabhan [60] and Nevell [61], and Kaverzneva, Ivanov, Salov and Kist [62] not only the primary alcoholic groups in cellulose molecules but also secondary ones undergo oxidation by dinitrogen tetroxide. Kaverzneva *et al.* have confirmed that N_2O_4 attacks primarily the carbon atom 6, oxidizing the groups CH_2OH to carboxylic groups.

Further, these authors assume that some carboxylic groups are formed by opening and oxidizing the pyran ring.

Oxidation of CHOH groups results, of course, in the formation of carbonyl groups, but the number of aldehyde groups formed is virtually nil. Kaverzneva and others have calculated that for every 100 anhydroglucose rings, 19 CO and 65 COOH groups are formed, but no more than 0.3 aldehyde groups. Such a product is unstable and tends to decompose readily in the presence of moisture or alkalis.

The content of nitrogen, which is all present in the form of ONO_2 groups, does not exceed 2.5% N.

Kenyon *et al.* [47] suggest that the action of dinitrogen tetroxide on cellulose proceeds in three stages:

(1) Nitric acid is produced by the chemical reaction of N_2O_4 and water, a small amount of which is present in the cellulose, formed in the course of oxidizing or nitrating cellulose:

$$2N_2O_4 + H_2O \longrightarrow 2HNO_3 + N_2O_3 \tag{5}$$

(2) Nitration of cellulose:

$$[C_6H_7O_2(OH)_3]_n + nHNO_3 \longrightarrow [C_6H_7O_2(OH)_2ONO_2]_n + nH_2O \tag{6}$$

(3) Hydrolysis of the cellulose nitrate produced and oxidation of the primary alcohol groups under the influence of nitrogen dioxide:

$$[C_6H_7O_2(OH)_2ONO_2]_n \xrightarrow{N_2O_4} [C_5H_7O_2(OH)_2COOH]_n \tag{7}$$

To show the effect of the percentage of dinitrogen tetroxide in the carbon tetrachloride solution on the nitrogen content and on the carboxyl group content of the reaction product, Kenyon reports the following data, collected in Table 84.

TABLE 84

N_2O_4:CCl_4 ratio	Nitrogen content, %	Content of carboxyl groups, %
1:1	0.32	21.1
1:2	0.33	12.8
1:3	0.35	9.3
1:4	0.37	7.6
1:5	0.39	7.4
1:6	0.40	7.0
1:7	0.40	6.3
1:8	0.39	5.9

The degree of cellulose oxidation decreases markedly as the concentration of N_2O_4 in the solution decreases. The nitrogen content, on the contrary, rises slightly as a result of the initial dilution, remaining constant during further decrease in concentration.

Other characteristics of the reaction of cellulose with nitrogen dioxide solution in carbon tetrachloride in the presence of anhydrous nitric acid, are shown in Table 85.

TABLE 85

Anhydrous HNO_3 parts	CCl_4 parts	N_2O_4 parts	Reaction time hr	Nitrogen content %	Content of carboxyl groups %
3.5	120	—	1	4.1	10.12
7.0	120	—	1	5.4	13.23
10.5	120	—	1	7.8	17.28
14.0	120	—	1	10.6	17.18
7.0	120	—	2	7.2	14.40
7.0	120	—	4	7.2	16.50
7.0	120	—	6	7.6	15.65
7.0	120	—	8	6.7	14.45
	60	60	2	0.58	11.94
	60	60	4	0.78	16.97
	60	60	6	0.76	19.33
	60	60	8	0.67	19.76
7.0	60	60	2	2.30	15.87
7.0	60	60	4	1.90	17.11
7.0	60	60	6	0.58	18.92
7.0	60	60	8	0.80	20.27

Cellulose oxidized by means of dinitrogen tetroxide can have surgical applications as a material for dressing wounds, since it is assimilated by the human body (Kenyon *et al.* [58]).

A nitrogen content of about 5.7% N can be attained after 1 hr on treating 5 parts of cellulose with 60 parts of dinitrogen tetroxide dissolved in 60 parts of carbon tetrachloride, mixed with 7 parts of anhydrous nitric acid. The relationship between the nitration time under the conditions mentioned above and the variation of nitrogen content of the product is shown in Fig. 128.

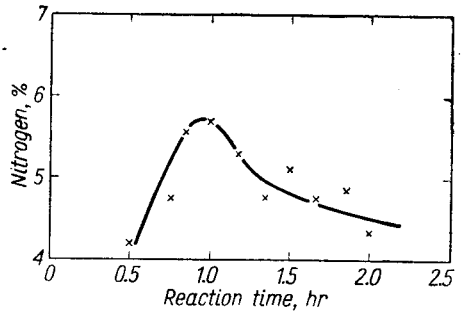


FIG. 128. Nitrogen content in nitrocellulose as a function of time of action with N_2O_4–HNO_3 solution. Ratio of reactants 5:60:60:7 (cellulose: N_2O_4: CCl_4: HNO_3) (Kenyon *et al.* [47]).

The shape of the curve indicates that after 1 hr, denitration begins.

Cellulose nitrated by fixed quantities of N_2O_4 and CCl_4, whilst the quantity of nitric acid varied from 0 to 40 parts, after one hour yielded products differing in nitrogen content. The highest nitrogen content was reached by adding 8–20 parts of nitric acid (Fig. 129).

Kaverzneva [63] and Nevell [61] have detected 1–1.5% of ketone groups (carbonyl groups), among the oxidation products of cellulose formed by oxidation of secondary alcohol groups.

The experiments cited are of great importance in practice. Mixed acids always contain a certain amount of nitrogen dioxide, hence the investigations described

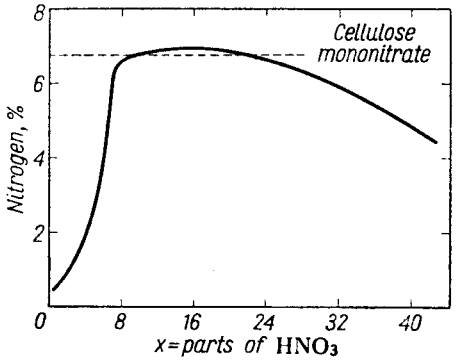


FIG. 129. Influence of the content of HNO_3 in nitric acid–N_2O_4 solution in CCl_4 on nitrogen content of nitrocellulose. Ratio of reactants 5:60:60: x (cellulose: N_2O_4:CCl_4:HNO_3) (Kenyon *et al.* [47]).

have disclosed the possibility that cellulose oxidation reactions may occur during nitrating. This may be regarded as confirmation of K. Smoleński's view (already mentioned, p. 229) that cellulose can be converted into pentosans through an intermediate stage involving uronic acids, more so, since it has been shown experimentally that the amount of pentosans could increase during nitration.

Celluronic acid nitrates (carboxycelluloses nitrates). Celluronic acid obtained by treating cellulose with nitrogen dioxide may then be esterified by means of nitric acid.

It has been found that even in the presence of a small number of carboxyl groups an appreciable change in the properties of the nitric ester is brought about, as compared with nitrocellulose.

To characterize the properties of the product obtained by esterifying celluronic acid with nitric acid, Rogovin, Treyvas and Shorygina [64] have reported the following numerical data, collected in Table 86.

These figures show that the nitric ester is scarcely soluble in a good solvent for nitrocellulose such as acetone when it contains 2 or 3% of COOH groups, i.e. one carboxylic group for 8–10 pyran rings.

In order to explain the low solubility of celluronic acid nitrates Rogovin *et al.*

TABLE 86

Carboxyl group content of the substance %	Nitrogen content %	Solubility in acetone %
1.56	13.5	18.2
3.6	13.0	9.7
8.0	11.5	13.2
18.5	7.0	2.5

suggest that cross-linkages are formed between the carboxyl and free hydroxyl groups, thus binding neighbouring molecular chains.

Due to partial substitution of the primary alcoholic groups by carboxyl groups, the strength of the glucosidic linkages joining the pyran rings is appreciably weakened, hence carboxycellulose containing 2–3% of COOH groups is de-polymerized if treated with dilute solution of alkalis even at room temperature.

NITRATION OF CELLULOSE IN THE GASEOUS PHASE

Investigations into the possibility of nitrating cellulose in nitric acid vapour on a commercial scale were first carried out by Deutsche Celluloidfabrik [65]. Later the process was described by Baker and Bateman [66]. The experiments were carried out as follows. Vapours of nitric acid, either at atmospheric pressure, or under reduced pressure of 20–90 mm Hg, or in a stream of carbon dioxide, were passed through a layer of cellulose at room temperature. None of these methods gave a product containing over 10% N, however, because the nitric acid was condensed on the cellulose fibres and gelatinized them. Better results were obtained by nitration with the vapours of nitrogen pentoxide in a stream of carbon dioxide, the products having a nitrogen content approaching 13.6% N. Even so, the surface of the fibres was gelatinized and the nitrated product was very non-uniform.

The next published paper was that of Berl and Rűff [67]. They treated cellulose by means of nitric acid vapours at 0°C for periods of 60–80 hr and attained a product containing only 4–8% N. From the X-ray diagrams, the authors concluded that a mixture composed of nitrated cellulose, non-nitrated cellulose, and Knecht compound (see p. 321) was formed. Later the question was investigated by Rogovin and Tikhonov [54] who subjected cotton to the action of vapours of 96% nitric acid. They have found that the time necessary to reach a specific nitrogen content by means of gaseous phase nitration was appreciably longer than that needed for nitrating in the liquid phase. Cellulose treated with liquid nitric acid of this concentration at 20°C yields a product of 12.65% N in $2\frac{1}{2}$ hr, whereas in the gaseous phase the same degree of nitration is scarcely achieved within 48 hr.

By nitrating cellulose by means of nitric acid vapours at pressures of 50–150 mm Hg and at temperatures from 38 to 65°C, Bouchonnet *et al.* [68] obtained products containing 10.9–13.7% N in periods of 15 min to 3 hr.

The most detailed research on nitration in the gaseous phase has been carried out by Wilson and Miles [69]. They concluded that there were no prospects of introducing this method in practice, since the nitrocellulose produced is non-homogeneous, and the nitration is inadmissibly slow. Thus, to reach a nitrogen content of 10% N by vapour phase nitration, at a vapour pressure of 16 mm Hg, a period of 48 hr was needed.

Similar conclusions have been reached by Champetier and Foëx [70] and by Trombe, Foëx and Champetier [71]. Wilson and Miles also studied the kinetics of nitration in nitric acid vapour. On the basis of these investigations they concluded that two molecules of nitric acid take part in the reaction with one OH group:

$$-OH + 2HNO_3 \longrightarrow -ONO_2 + HNO_3 \cdot H_2O \qquad (8)$$

Acid of the composition $HNO_3 \cdot H_2O$ is a strong denitrating agent and this may account for the difficulty in obtaining a highly nitrated product when using HNO_3 vapour. Instead of the ordinary equation of the second order

$$\frac{dx}{dy} = Ky^2$$

Wilson and Miles suggest the following second order equation for the rate of nitration with nitric acid in vapour phase:

$$\frac{dx}{dy} = K(y-r-s)^2$$

where s is the acid combined with the water formed and present in the fibre and r is a correction for the absorptive capacity of the nitrate groups in the cellulose, deduced from the determined absorption of nitric acid by fully nitrated cellulose.

Shoryghin and Khait [57] brought cellulose into contact with vapours of nitrogen dioxide at room temperature and obtained a product largely oxidized and degraded, that contained up to 3.2% N.

Dalmon [72] reacted the fibre of Chinese nettle (ramie) with nitric anhydride in a stream of dry air. Nitrocellulose containing as much as 14.12% N, i.e. cellulose trinitrate (within the limits of analytical error), was obtained. T. Urbański and Janiszewski [56] obtained a nitrogen content of 13.90–13.95% on repeating these experiments with cotton (linters) at 25°C.

The nitration of polysaccharides with nitrogen pentoxide in the gaseous phase has the advantage of not degrading the large molecule (Vollmert [73]).

During World War II, a method of two-stage cellulose nitration was used in Germany on a semi-plant scale (10 tons a month). Cellulose was first treated with air saturated with nitric acid vapours, and then the partially nitrated cellulose was immersed in 98% nitric acid. The initial treatment of the cellulose with vapours of nitric acid prevents the surface gelatinization that ordinarily occurs if cellulose is introduced direct into concentrated nitric acid. The product obtained in this way

contained 13.65–13.8% N, and was very easy to stabilize since no sulphuric acid had been used in the nitration process.

According to a description by Buhs [74] the method was developed by Dietsch, Mesket and Hechler. See also [84].

NITRATION WITH NITRONIUM CHLORIDE

T. Urbański and Siemaszko [75] examined the nitration of cellulose with NO_2Cl in the vapour phase. Gaseous NO_2Cl was drawn through cellulose at 20°C for 4 hr, and the nitrocellulose than subjected to the usual treatment. A product with 12.2% N was obtained with 168% yield. The product does not contain chlorine. Its stability is higher than that of nitrocellulose of the same nitrogen content prepared by means of the usual nitrating mixture.

It is interesting to note that NO_2Cl dissolved in chloroform or carbon tetrachloride was a much less efficient nitrating agent and only yielded a product of 9.5–10.0% N.

KINETICS OF NITRATION. HEAT OF REACTION

It was demonstrated in the early investigations of Lunge [15] and Berl [31] (see pp. 327 and 341) and more recent work of Chédin and Tribot [76] on the nitration of cellulose that the nitration reaction proceeds very rapidly for the first few minutes, whereupon the rate decreases gradually, slowing down as the maximum nitrogen content is approached. At 20°C and above, this stage is reached within 20 min.

A striking example of the great rapidity of nitration, particularly in the first few minutes can be seen from the diagram by Spalding [76a] (Fig. 130). The figures

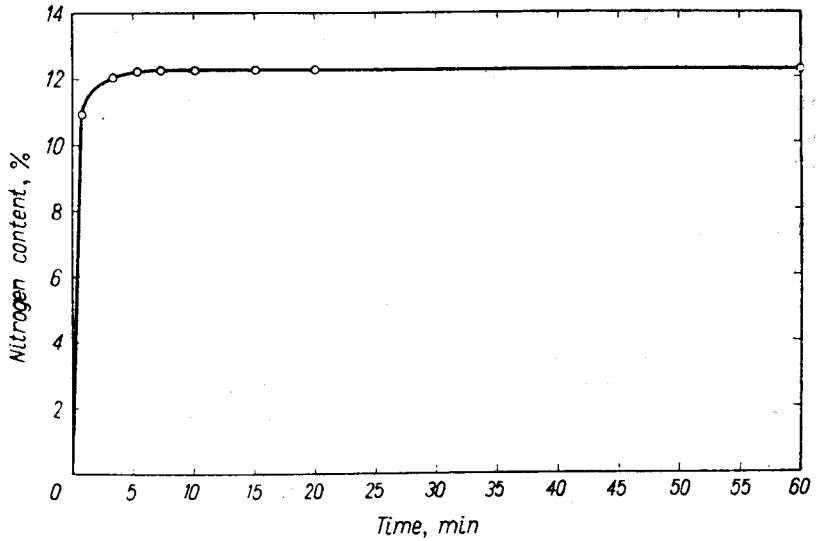


FIG. 130. Rate of nitration of cellulose in a laboratory dipping pot, according to Spalding, Hercules Powder Co. [76a].

refer to the nitration of cellulose with a mixed acid containing 21.0% HNO_3, 61.5% H_2SO_4 and 17.5% H_2O.

At a lower temperature the process is slower. Hence in order to bring about a thorough nitration in a short period, a more concentrated nitrating acid should be applied. The rate of nitration depends not only on the composition of the mixed acid and its temperature, but also on the rate of diffusion of the acid within the cellulose fibre.

Atsuki and Ishivara [77] have established that the rates of diffusion and of esterification are of the same order, but that diffusion proceeds more rapidly.

According to Sakurada [78] bleached cellulose is nitrated in a shorter time than an unbleached one since diffusion through the bleached tissue is quicker. Nitration was carried out at 0°C by means of a 1:2 mixture of nitric acid, density 1.52 g/cm^3 and sulphuric acid, density 1.84 g/cm^3. The results are shown in Table 87.

TABLE 87

THE EFFECT OF NITRATING BLEACHED AND UNBLEACHED COTTON (AFTER SAKURADA [78])

Bleached ramie-cellulose			Unbleached ramie-cellulose		
Time of nitration sec	Nitrogen content of nitro-cellulose %	Nitrate group number in one $C_6H_{10}O_5$ unit	Time of nitration sec	Nitrogen content of nitro-cellulose %	Nitrate group number in one $C_6H_{10}O_5$ unit
—	—	—	15	1.53	0.20
45	3.18	0.42	45	2.11	0.27
90	3.91	0.52	90	2.71	0.35
300	5.63	0.78	300	4.55	0.61
600	7.67	1.18	599	5.86	0.82
1800	11.07	2.00	1800	9.08	1.49
3600	12.65	2.48	3600	11.82	2.20
18,000	13.85	2.89	18,000	13.80	2.87

Taking into consideration the factor of diffusion Sakurada expresses the nitration rate of cellulose by the equation

$$x = kz^m$$

where: x is the amount of cellulose that has entered into reaction, z — the time of reaction, k, m — constants depending on the capacity of the acid to diffuse into the fibre. The kinetics of nitration of cellulose in nitric acid vapour was reported earlier (p. 354).

Recently Kunz *et al.* [79a] examined the nitration of pulverized cellulose and found it to be extremely rapid.

To emphasize the importance of diffusion into the solid phase as a factor affecting the nitration of cellulose, an observation of Hackel and T. Urbański [79] (see

p. 428) may be cited. Thus the nitration of starch by means of mixtures rich in nitric acid results in a higher nitrogen content than obtained from cellulose under corresponding conditions, because the starch is dissolved in such acids. (This has already been discussed on p. 341.)

A new concept of the mechanism of O-nitration of cellulose and denitration of nitrocellulose was recently advanced by Trommel [80]. On the basis of his experiments on the nitration equilibrium of cellulose he came to the conclusion that various reacting groups in cellulose and nitrocellulose molecules differ in their accessibility to nitration and denitration respectively.

The accessibility of the OH groups in cellulose is 96–99% when nitrated with mixed acids. The accessibility of ONO_2 in cellulose trinitrate on denitration is only *ca.* 70%. The latter value is much lower than the former because of the much higher crystallinity of the trinitrate compared with that of the lower substituted cellulose nitrates. The difference may explain why the rate of nitration is higher than that of denitration. The inaccessible regions in the nitration are to be attributed to cellulose "junction points" and in the denitration of cellulose trinitrate to trinitrate "junction points".

On the basis of his studies on the kinetics of the O-nitration of cellulose, Miles [8] concluded that the reaction of O-nitration of cellulose should be expressed as follows:

$$-OH + 2HNO_3 \rightleftarrows -NO_3 + HNO_3 \cdot H_2O \qquad (9)$$

the water produced during the nitration being combined with a molecule of nitric acid.

Hence the equilibrium value can be expressed by the equation

$$K_1 = \frac{[-NO_3][HNO_3 \cdot H_2O]}{[-OH][HNO_3]^2} \qquad (10)$$

Nitric acid hydrate exists in balance with its components. Therefore there is a further equilibrium value:

$$K_2 = \frac{[HNO_3 \cdot H_2O]}{[HNO_3][H_2O]} \qquad (11)$$

Thus the final total equilibrium value of the process is expressed by the ratio

$$K = \frac{K_1}{K_2} \qquad (12)$$

According to other investigations (Sendo [25], Kagawa [26]):

$$K = \frac{a_w}{a_n} \cdot \frac{a}{3-s} \qquad (13)$$

where: a_n – the activity of nitric acid, i.e. the ratio of the vapour pressure of the nitric acid in the mixture to that of pure nitric acid;

a_w – the activity of water, i.e. vapour pressure ratio of the water in the mixture to that of pure water;

s – the number of nitrated hydroxyl groups for every C_6, in which for every anhydroglucose unit there are $3 - s$ non-nitrated groups.

Heat of nitration. During O-nitration of cellulose heat is evolved. Wilson, in 1937 [81] first carried out measurements of the thermal effects of this reaction with both nitric acid–water, and mixed acid.

The results of his measurements (in cal/g of cellulose) are summarized in Table 88.

TABLE 88

Final percentage of nitrogen %	Total heat evolved during nitration	Heat developed due to the change in acid composition		Heat of absorption by nitrocellulose	Heat of nitration (and $-\Delta H_n$ kcal/mole HNO_3)
		$-HNO_3$	$+H_2O$		
10.57	69.3	−10.1	33.0	26.7	19.7 (1.74 kcal /mole HNO_3)
13.28	111.4	−13.1	64.2	13.8	30.5 (1.86 kcal/mole HNO_3)

Kagawa [82] established that the heat of nitrating cellulose to 10.4% N is 77.5 cal per 1 g cellulose, from which he calculated the heat of nitrating one —OH group to be 2.11 kcal. Calvet and Dhers-Pession [83] reported a value of 2.0 ± 0.2 kcal.

Kunz *et al.* [79a] determined the heat of nitration of pulverized cellulose at 0°C with nitric acid. They found it be 61.6 cal per 1 g cellulose or 1.696 kcal per one nitrated OH group.

The heat of nitration has been also calculated from the heat of combustion of nitrocellulose (Miles [8]), as 1.17 kcal per one hydroxyl group. Measurements of the heat of combustion are extremely accurate, hence this value appears to be close to the actual value although it differs considerably form the values obtained by direct measurement by earlier authors.

Temperature coefficient of nitration. Experiments have shown that in a moderate range, e.g. from 0 to 45°C, temperature affects the degree of nitration very little. A decrease in temperature usually results in some decrease in degree of nitration on a technical scale, where nitration time is limited, but this is because equilibrium is not reached, and the rate of the reaction is the governing factor. From a knowledge of the heat of nitration it should be possible to predict the course of the reaction from the known equation:

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2} \tag{14}$$

However, the experiments by Miles [8] do not confirm these thermodynamic calculations, due to our incomplete and faulty knowledge of the mechanism of the nitration reaction.

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CHAPTER XIII

NITROCELLULOSE MANUFACTURE

PREPARATION OF CELLULOSE MATERIALS FOR NITRATING

IN THE following section information is given about the industrial methods of obtaining cellulosic raw materials, such as cotton and wood pulp cellulose, for the purposes of nitration. The question is discussed more extensively in special handbooks devoted to the technology of cellulose. For this reason the description that follows will be limited to general information only.

The basic sources of raw material for the manufacture of cellulose are cotton, and wood cellulose.

COTTON

Cotton is the richest source of cellulose, since cotton fibres contain as much as 85–97% cellulose. Cotton consists of the nap covering the seeds of the cotton plant (*Gossypium*) which grows throughout the whole year in a warm, moderately damp climate (Egypt, southern areas and of United States, and U.S.S.R., India, and China Pacific Islands). The length, thickness and colour of the nap depend on the variety of the plant and on the climate in which it is cultivated.

Every cotton fibre consists of a single cell, filled with air and albumin residues, breakdown products of protoplasm. It also contains certain colouring matter.

Two kinds of cotton are obtained from the cotton plants:

1. Long fibre cotton 20–50 mm in length and 0.01–0.04 mm dia., which is the raw material for the textile industry. Waste from this cotton is utilized in the production of certain sorts of high viscosity nitrocellulose, e.g. dynamite nitrocotton.

2. Short fibre cotton, 10–20 mm in length, known as linters, which is the nap remaining on the surface of the cotton seeds after the long fibres of cotton destined for spinning have been separated. Short cotton fibres are separated from the seed by special machines and compressed into bales so as to reduce the bulk of the product to be sent for purification.

The purification of linters consists in removing all non-cellulosic substances, such as fats and waxes, lignin, proteins, non-cellulosic carbohydrates and mineral substances. The process is carried out in two stages:

(a) mechanical cleaning and (b) chemical purification.

The mechanical cleaning consists in passing the linters through toothed rollers, which remove the large types of foreign body. Thus the cotton is teased out on the rollers and transported by conveyer to autoclaves in which it undergoes chemical purification under pressure.

Linters in batches of about 3000 kg are kiered in a 1–3% solution of caustic soda for a period of 2–6 hr, at a temperature of 105–140°C. The access of air must be prevented during this operation. During kiering the fats and waxes are hydrolysed, pectins are decomposed, and at the same time hydrolysis and dissolution of the residual lignin in the chaff takes place. The duration and the temperature of treatment depend on the cleanness of the linters, and must also be correlated with the viscosity desired in the product. The higher the temperature and the longer the time of boiling the lower the viscosity of the cellulose produced and hence that of the nitrocellulose. After kiering is finished a large valve in the bottom of the autoclave is opened, the hot mass being expelled by the pressure within the autoclave into a double-bottomed tank. The upper false bottom acts as a strainer, on which the cotton is rinsed with a large amount of water until all traces of sodium hydroxide are removed. About 150 m^3 of water are consumed for 1 metric ton of linters.

The colour of cotton purified in this manner is pale to dark brown. The product is then bleached by means of chlorine or hypochlorite solutions at room temperature. Vats provided with a vertical stirrer or trough-shaped vessels with a horizontal or vertical stirrer are usually used for this purpose.

During chlorination, destruction of the colouring matter and further decomposition of other substances accompanying the cellulose proceeds, all these substances being oxidized by chlorine or hypochlorite.

The bleached cotton is thoroughly washed with water to remove residual chlorine and its compounds and then the alkalis are neutralized by acidifying with dilute sulphuric acid. The product is then rinsed again with water to remove the mineral constituents.

If the linters are to be used for the manufacture of particularly pure, white collodion cotton intended for production of varnishes or celluloid, it is necessary to remove any iron compounds from the cellulose. This can be carried out by washing the cotton with an oxalic acid solution, followed by a water rinse.

The results achieved by linters purification are shown in Table 89.

The moisture content of the raw linters is 5–10% depending on the climate of the country in which it is stored.

In general, linters are considered the best raw material for nitrocellulose manufacture, having the following advantages as compared with long-fibre spinning cotton: (a) low price, (b) easier handling, (c) shorter time of pulping the product preceding stabilization. The advantages (b) and (c) result from the fact that the linters are composed of short fibres.

If long-fibre cellulose is to be used as a nitration material then noils from combing machines or waste from a spinning mill are usually used. Such wastes are usually contaminated with lubricating oils and before the chemical treatment they should be

TABLE 89
THE EFFECT OF PURIFYING LINTERS

Components	Raw linters %	Purified linters %
α-Cellulose	75–85	99.0
Fats and waxes	0.5–1.0	0.2
Proteins	1.0–1.5	0.2
Mineral components (including iron compounds)	(0.06)	(0.002)
Hemicelluloses	5	0.3
Lignin	3	0.2

subjected to an extraction with petrol or other solvent, e.g. trichloroethylene or carbon tetrachloride. Subsequently they are boiled for a short period in dilute caustic soda solution so as not to lower the viscosity, since cotton with long fibres is used for manufacturing nitrocellulose of the highest viscosities. For the same reason such cotton is not usually bleached.

During alkaline kiering and bleaching, cellulose does not undergo purification only. Simultaneously a certain modification of its tissue takes place: it grows more spongy and permeable, and is therefore able to take up rapidly liquids such as mixed acid. This makes the process of nitration considerably easier.

In commercial specifications for cotton destined for nitration, the following approximate values are required:

moisture percentage	*ca.* 6%
mineral (as ashes), up to	0.5–0.7%
fats and waxes in average up to (oily places can contain up to 1%)	0.30%
mechanical impurities (determined by hand sorting of a sample) up to	0.01–0.02%
organic impurities, undergoing carbonization by conc. sulphuric acid, and insoluble in this acid, up to	0.75–1.0%
chlorine, free	absent
chlorine, bonded, determined in ash, up to	0.05%

WOOD CELLULOSE

The question of substituting wood pulp cellulose for cotton as a raw material in the production of nitrocellulose arose at the beginning of the present century due to the big increase in nitrocellulose manufacture, which was followed by an expansion in the demand for cotton.

A particularly acute shortage of cotton occurred in Germany during World War I, and wood pulp cellulose was widely used there for nitration, although the product was inferior in quality than that made from cotton. Towards the end of World War I (about 1918), due to the shortage of cotton in the U.S.A. (despite

the very large production there), attempts were made to nitrate wood cellulose. They were accompanied by serious difficulties. It was found that wood pulp in the form of crepe paper tended to swell significantly in the course of nitration. After nitration the product retained much more acid than nitrocotton, while the yield of nitrocellulose was smaller, since from 100 parts of cellulose 120 instead of 150 parts of nitrocellulose were obtained. Nitrocellulose made from wood pulp and intended for powder manufacture, when dehydrated with alcohol, gave up its water with difficulty owing to its peculiar fibrous structure. Therefore, during the transition period the nitration of mixtures of linters and wood cellulose was widely practized in many countries. The mixtures are still in use for some rocket propellants where high mechanical properties are required.

Eventually, the problem of using wood cellulose as a nitration material was solved successfully during the interwar period, and during World War II, wood pulp cellulose was commonly used for nitrocellulose manufacture.

Raw wood contains 45–60% of cellulose. Morphologically this kind of cellulose is distinguished from cotton cellulose by the smaller size of its fibres. Chemically it is more reactive.

Spruce wood for example consists of the following components:

cellulose	55–56%
carbohydrates, other than cellulose	10–14%
lignin	20–30%
oils, resins, mineral matter	13–15%
albumins	0–0.7%

The separation of cellulose from the wood is carried out by one of three methods: the soda process, the sulphate process, and the sulphite process. Nitration cellulose is prepared chiefly by the sulphite and sulphate methods.

In the sulphite pulping process wood cut into pieces is subjected to kiering in a calcium bisulphite solution under a pressure of 3–8 kg/cm^2, at 120–145°C for 7–30 hr. The higher the temperature, the shorter the time of boiling. Substances accompanying cellulose dissolve in the liquor. Lignin is converted into a soluble lignin sulphonic acid. Cellulose is isolated from the solution, known as sulphite cellulose lye, and washed with water.

The sulphite process produces cellulose pulp readily bleached, pale in colour, containing a high percentage of α-cellulose and a low content of lignin and of pentosans. The large quantities of waste sulphite cellulose lye obtained as a by-product can be used for various purposes, i.e. alcoholic fermentation, production of fodder yeast, manufacture of tanning agents, production of vanillin, etc. Nevertheless, sulphite lyes in general cause much trouble, since the amount of liquor produced is usually larger than can be rationally utilized.

The average composition of crude cellulose sulphite pulp is as follows:

cellulose	85%
lignin	2%
pentosans	4%
hexosans	5%

The "sulphate" process consists in kiering pieces of wood in a solution composed of sodium hydroxide, sodium sulphide and sodium carbonate in a 65:15:20 ratio. The concentration of the solution is 10–12% of NaOH. Boiling at a temperature of 170–175°C under pressure lasts about 6 hr, of which 3 hr are required for heating, the other 3 hr being the kiering proper. Cellulose is then separated from the lye, washed with water, bleached, and subjected to final purification. The lye is condensed, evaporated to dryness, then sodium sulphate is added, and the whole is calcined. The sodium sulphate is thus reduced to sodium sulphide. Unchanged sulphate and the excess of carbonate are removed by addition of milk of lime.

The sulphate process yields cellulose pulp of high purity, though it contains more lignins. This pulp has a darker colour and does not undergo bleaching so readily. This is probably due to the presence of relatively stable, coloured sulphur compounds. Further, the content of undecomposed pentosans is higher in the sulphate pulping process than in the sulphite method. One of the advantages of the sulphate method lies in the recovery of the whole "sulphate lyes". When coniferous trees are used, certain amounts of turpentine and of "sulphate oil" ("tall oil") are also obtained.

Cellulose for nitration is subjected to bleaching and to final purification.

Bleaching. Crude wood cellulose is bleached by means of calcium or sodium hypochlorite in large tanks, "bleachers", equipped with stirrers. Bleaching cellulose is of great importance for nitrocellulose manufacture, particularly in the case of nitrocellulose intended for the production of smokeless powder. It is essential that the powder should be pale in colour, as a change in the colour of the powder often indicates decomposition. Similarly, cellulose destined for manufacturing collodion cotton, for varnishes, celluloid and film, should be carefully stripped of colour so that the final products are colourless.

Finishing wood cellulose. The finishing process is made to obtain a higher α-cellulose content and to endow the wood pulp with a shape conducive to easy nitration. This is the last operation prior to nitration. It consists in removing hemicelluloses, pentosans, and hexosans, which are undesirable ingredients of wood pulp. An insufficiently purified wood pulp may contain 5–6% of pentosans, straw cellulose even as much as 20%, whereas cotton does not contain more than 0.5–0.6%.

According to the present theory (e.g. Zherebov [1]) most of the hemicelluloses, pentosans and hexosans are removed during sulphitation, because calcium sulphite is capable of forming addition compounds with pentosans. Complete removal of hemicelluloses is only possible however after lignins have been removed, as lignin seems likely to be chemically combined with hemicellulose and thus with pentosans or hexosans. Only rupture of these bonds and the separation of lignins makes it possible to attack the non-cellulosic polysaccharides (Heuser and Haug [2]).

Generally after each operation including bleaching, the cellulose is washed with sodium hydroxide solution, so as to increase the content of α-cellulose.

The final purification is designed chiefly to remove pentosans, as these undergo nitration with difficulty to yield products of low nitrogen content that are insoluble or only partly soluble in organic solvents. Hence the presence of pentosans can

have an adverse effect on the nitrogen content and solubility of the nitrated product. The imperfect solubility causes the solutions to be turbid, which is particularly detrimental in nitrocellulose for manufacturing varnishes and films.

A high proportion of lignin also reduces the solubility of nitrocellulose. According to Bryde and Rånby [3], the solubility in acetone is reduced only when the lignin content approaches 18%.

The physical nature of nitration cellulose is very important. In general it is prepared in the form of thin paper sheets, 16–20 g/m^2 in weight. It is also possible to produce wood cellulose in the form of loosened fibres resembling linters by "carding", i.e. tearing cardboard in two opposite directions.

The form of the cellulose affects its permeability to acid, and the retention of spent acid in the fibres. Schur and McMurtrie [4] report that wood pulp cellulose from coniferous trees retains the more acid, the larger the diameter of the cellulose fibres.

An extensive discussion, explaining which forms of cellulose are the most suitable for nitrating, appears in a paper by Schur and Hoos [5].

In Great Britain, according to the patents of Picton [6] small flakes of sheet wood-cellulose have been nitrated, while in the United States shredded cellulose prepared by the Stern method [7] was most widely used (shreds made of loosely felted cellulose fibres in a special machine). This last form of cellulose is especially suitable for uniform penetration and imbibition of the nitrating acid. Normal nitrators, as used for linters, are also suitable for nitrating this type of cellulose.

Wood pulp for nitration is made exclusively from coniferous trees, since it has been found that conifers give cellulose with long fibres, and hence mechanical losses are small.

OTHER SOURCES OF CELLULOSE

In the view of the limitations governing cotton growing and the necessity of preserving existing areas of woodland, the problem of finding alternative sources of cellulose for nitration other than cotton or wood cellulose, has received attention. To solve this question investigations were made at the turn of the present century, and later during World War. I. Experiments on the nitration of cellulose fibres from maize stalk, agave, hop, hemp, flax, alfalfa and ramie, have been described. The majority of these experiments were devoted to the nitration of expensive fibres, of high value in the textile or paper industry. It is clear that work of this kind could not receive great attention due to economic considerations, and the experiments were limited for the most part to the laboratory scale.

More important, from the practical point of view, was the extensive work of Pšenica [8] devoted to the question of nitrating fibres of cellulose isolated from nettle, fibres of little interest for the textile industry. By nitrating nettle cellulose in the same way as cotton, nitrocellulose containing 13.4% of nitrogen was produced, of adequate chemical stability provided the cellulose was well purified before the nitration.

Another cheap and readily available source of cellulose is the straw of annual plants. This raw material usually contains exceptionally large quantities of mineral matter. In order to separate cellulose the chlorine process is often used. It consists in treating the cellulosic raw material (previously boiled in a 10% sodium hydroxide solution and then in water) with chlorine. The decomposition of lignin, pentosans and other substances takes place and at the same time the cellulose is bleached. Crude cellulose prepared in this way contained 80–92% of α-cellulose and about 1% of mineral matter.

Naiman and Troitskii [9] have carried out extensive investigations to compare the nitration of cotton with that of cellulose differing in origin and purity from wood pulp, with hydrocellulose and oxycellulose, and with pentosans. The results are collected in Tables 90 and 91.

TABLE 90

COMPOSITION OF DIFFERENT CELLULOSIC RAW MATERIALS FOR NITRATION

No.	Material for nitrating	Cellulose content %	Copper number	Pentosans content %	Lignin content %	Fats, waxes content %	Ash content %
1	Cotton cellulose	99.55	0.06	—	—	—	0.08
2	Wood cellulose	98.50	0.59	1.38	0.36	0.23	0.20
3	Surgical cotton	98.86	0.49	1.43	0.37	0.24	0.12
4	Linters	99.38	0.13	2.14	0.10	0.37	0.36
5	Purified wood cellulose	96.08	0.29	2.90	0.02	0.21	0.44
6	Bleached wood cellulose	87.36	1.20	5.63	0.77	0.91	0.29
7	Unbleached wood cellulose	87.76	1.10	4.86	4.23	1.22	1.30
8	Bleached spruce paper	86.64	1.13	4.77	0.55	0.41	0.54
9	Unbleached spruce paper	87.90	1.14	4.93	1.61	0.57	0.88
10	Straw cellulose, bleached	71.96	1.39	27.45	2.78	0.27	3.25
11	Spruce sawdust	60.45	2.4	10.92	29.26	7.27	0.16
12	Cotton hydrocellulose	93.45	3.91	1.31	—	0.18	0.49
13	Oxycellulose	69.72	8.91	1.09	0.12	0.10	0.76
14	Pentosans	—	—	90.75	—	—	0.47

Nitration was carried out with acid of composition:

22.2%	HNO_3
68.5%	H_2SO_4
9.0%	H_2O
0.3%	NO_2

The ratio acid: cellulose was 60. The nitration was carried out for 1 hr at 15–18°C.

From the values obtained the deleterious effect of pentosans is noticeable since the presence of these compounds reduces the yield and the solubility of the product. The adverse effect of a high percentage of pentosans is less evident when only lower

TABLE 91

THE RESULTS OF NITRATING MATERIALS LISTED IN TABLE 90

No.	Nitrogen content %	Solubility %		Viscosity	Ash %	Yield %
		in ether–alcohol	in alcohol			
1	13.1	—	—	—	—	171.1
2	13.1	18.9	0.51	1.1	0.04	163.3
3	13.2	1.6	0.27	23.2	0.14	—
4	13.15	3.3	1.03	7.3	0.11	167.5
5	13.1	4.0	0.18	8.1	0.7	167.0
6	13.0	7.0	0.62	10.0	0.20	163.2
7	12.95	8.8	0.35	10.0	0.33	153.5
8	12.95	8.3	1.26	6.5	0.12	—
9	12.95	8.6	0.97	9.4	0.07	—
10	12.55	9.5	1.86	5.4	0.3	132.1
11	11.7	14.8	2.33	4.8	0.3	96.0
12	13.2	17.5	—	1.4	0.11	151.9
13	12.8	5.5	1.72	—	0.6	140.3
14	10.7	17.3	3.5	—	0.4	102.5

nitrated products are produced, probably because pentosans treated with less concentrated acids are decomposed by oxidation and hydrolysis, and dissolve in the acid.

Oxycellulose produces a product difficult to stabilize, in low yield. Hydrocellulose, on the other hand, yields a product more soluble in ether–alcohol mixture, and containing more nitrogen than the nitrated oxycellulose.

From their experiments Naiman and Troitskii concluded that wood pulp cellulose should be subjected to specially careful purification before nitration.

More recently attempts to nitrate viscose fibres have been reported, e.g. Newman [10], Okajima, Hayama, Watanabe [11] nitrated viscose fibres by means of a mixture containing nitric acid and acetic anhydride.

DRYING CELLULOSE BEFORE NITRATION

Cotton or wood pulp as delivered to nitrocellulose plants contains 6% or more of moisture. This moisture should be removed prior to nitration so that it does not bring about any dilution of the mixed acid and thereby change the course of the reaction. Cotton is usually transported in the form of compressed bales, which are opened and shredded before drying. Wood cellulose, in the form of pressed cellulose pulp or of crepe paper, is dealt with similarly. Dryers for dehydrating cotton or cellulose may be of various types. The simplest is the shelf drier, equipped with mechanical ventilation and heaters situated at the bottom, supplied with water or steam so as to maintain a temperature of 80–100°C inside the drier.

More thorough and quicker drying is attained in the formerly widely used Schielde

semi-continuous driers. A simple design of this type of drier is shown in Fig. 131. It comprises two drying chambers I and II, separated by partitions. The whole is made from sheet-iron. In the lower part of one chamber and between the chambers heaters are installed. Air sucked from above by means of a ventilator enters one of chambers (I) from underneath and is heated there. Flowing upwards, it passes a range of shelves on which cellulose material is spread. Subsequently the air passes

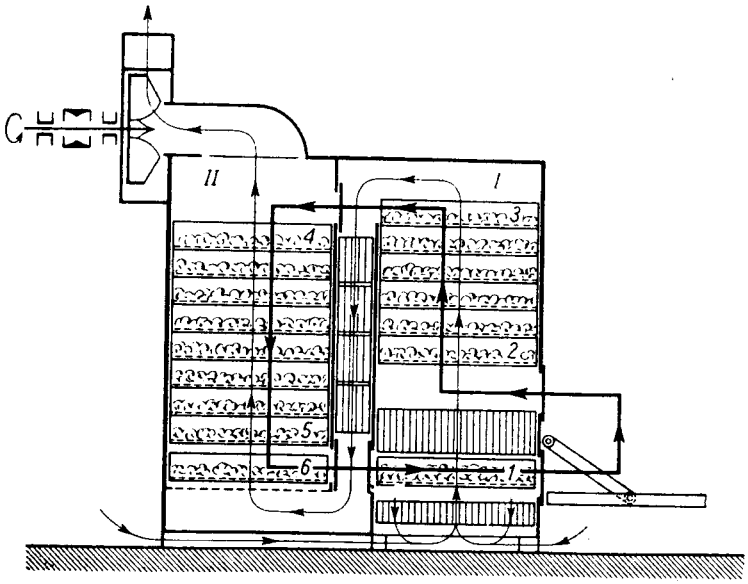

FIG. 131. Schielde drying oven for cellulose.

via the central heater to the other chamber (II), where again it flows upwards and escapes through a ventilator.

Cotton or wood cellulose is introduced into an iron box *1* equipped with a metal mesh bottom occupying the outside position. By means of a chain and sprocket mechanism the box is moved in position *2* and later to the position *3*. Meanwhile another box *1* is loaded and so on. Finally the box from position *3* is transferred to the neighbouring chamber, position *4*, to be shifted gradually downwards to the positions *5* and *6*, and thereafter to the position *1* and outside again. There the dried cotton is unloaded and replaced by a fresh batch. Drying cellulose in chamber (I) is co-current process, while in the chamber (II) a counter-current process is carried out. The movement of shelves carrying the cellulose is marked as a thick line, while a thin line indicates the direction of air.

A continuous drier of the Petrie type is outlined in Fig. 132. This drier is a sheet-iron box about 4.5 m high, about 6.0 m long, and 1.25 m wide. In this box five or six slatted shelves are constructed. Between the slats a system of movable slats is arranged so as to propell the cotton in one direction, by a series of upward and forward movements. After each forward movement the slats are lowered and return

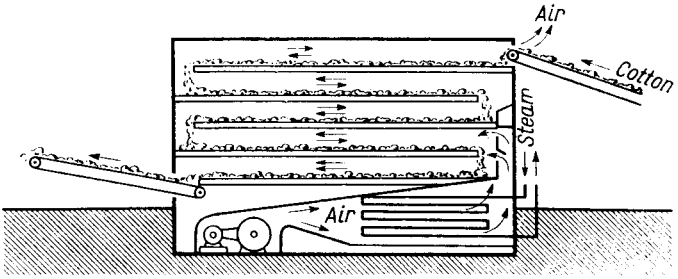

FIG. 132. Petrie drying oven for cotton.

to their original position, to repeat the cycle. In this way wet material falling from a conveyer onto the uppermost shelf of the drier is gradually pushed towards the lower shelves, till it ends on the bottom conveyer which removes the dried material.

Air, blown through a steam heater situated in the lower part of the drier, is warmed and then flows to the upper part of the unit in co-and counter-current with the cotton. It has been found that application of the counter-current principle can readily cause a blockage in the lower part of the drier.

The Petrie drier is unsuitable for drying wood pulp in the form of thin paper sheet, as such a material is readily carried away by the air stream, the mechanical device alone is not sufficient to shift cellulose of this sort.

Among other systems of driers, continuous apparatus transporting cellulose on a conveyor belt in a stream of warm air are widely used (Fig. 133).

During World War II pneumatic driers of cellulose were developed in Germany and they are in use in modern industrial practice. They are based on the

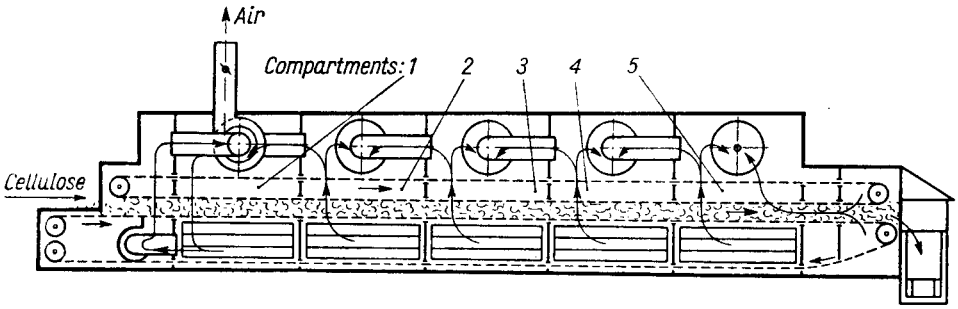

FIG. 133. Diagrammatic presentation of Hass drying oven [12].

principle of introducing cellulose into a stream of hot air. Air is heated to 110°C and cools down to 80–90°C when contacting cold cellulose with the normal moisture content (6–8%). The stream of air with cellulose enters "a cyclone" where the air velocity is rapidly reduced and the cellulose falls down. A diagrammatic presentation

of pneumatic drier is given in Fig. 134. Air filtered through (*1*) is blown by a fan (*2*) into a heater (*3*). Cellulose enters (*4*) and passes with air along the wide pipe to a cyclone (*5*). From here moist air leaves (*6*) and dried cellulose falls through (*7*).

The advantage of pneumatic driers is that they serve both for drying and transporting the cellulose. Drying is very quick.

The disadvantage of the method is that it is difficult tolower the moisture content below 2% (this is the consequence of the co-current system). Also the air consumption

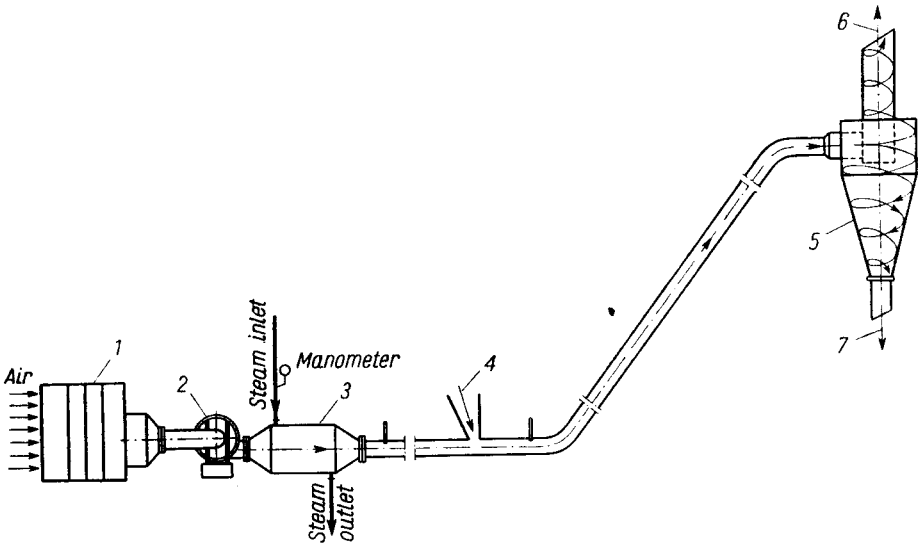

FIG. 134. Cellulose drier with a pneumatic transport [12].

is high (*ca.* 10 m^3/kg of cellulose). This is much higher than in ordinary mechanical driers.

Cellulose material, such as cotton or wood cellulose, is dried until the moisture content is below 1%, or in the pneumatic drier to *ca.* 2%, and then loaded into sealed sheet metal containers or bags, to cool to room temperature.

Care should be taken that the temperature inside the driers does not exceed 105–110°C, as otherwise the material may ignite. Further, there exists a danger of inflammation of the cotton dust present in the air, for it can be kindled by static electricity. For this reason both the driers and all auxiliary equipment must be earthed.

INDUSTRIAL NITRATION OF CELLULOSE

The types of nitrocellulose produced commercially and their properties are listed in Table 92.

Data on the viscosity of different types of nitrocellulose, particularly varnish nitrocellulose have been given above (see p. 277).

TABLE 92

TYPES OF NITROCELLULOSE

Nitrogen content %	Amount of NO cm^3/g subst.	Solubility	Name of nitrocellulose type	Specific gravity
13.45–12.9	214	Insoluble both in alcohol and in ether–alcohol, soluble in acetone and ethyl acetate	Guncotton, coton-poudre No. 1, (CP_1), nitrocellulose No. 1 (NC_1), Schiessbaumwolle S (13.2–13.4% N)	1.659–1.654
12.6–12.8	203	Partly soluble in ether–alcohol	Pyroxyline, pyrocollodion cotton, pyrocellulose	1.653
12.3–11.0	196–176	Soluble in: ether–alcohol, acetone, ethyl acetate, insoluble in alcohol, soluble in nitroglycerine	Collodion cotton (colloxyline), coton-poudre No. 2 (CP_2), nitrocellulose No. 2 (NC_2), Schiessbaumwolle PE (11.3–12.6% N)	1.653
10.5–10.0	162	Soluble in alcohol and other organic solvents	Low-grade collodion cotton	

MIXED ACIDS

Clearly composition of the nitrating acids used to nitrate cellulose depends on the type of nitrocellulose required. Nitrocellulose showing specific properties can be produced by means of mixed acid of widely different composition. Hence the composition of the nitrating acid should be chosen to secure the most advantageous operating conditions, as for instance the most economic mixture with the highest safety factor during nitration. The use of mixtures of high nitric acid content increases the risk of the product igniting during nitration.

In practice the H_2SO_4 to HNO_3 ratio ranges from 2.5–3, while the water content should be varied according to the required degree of nitration, the solubility of nitrocellulose, etc.

For manufacturing high nitrated guncotton (coton-poudre No. 1 or CP_1 in France, Schiessbaumwolle S in Germany) the mixed acid should contain 5–13% of water. For the production of lower nitrated guncotton (coton-poudre No. 2 or CP_2 in France, Schiessbaumwolle PE in Germany) 15–20% of water is used and for collodion cotton 18–25%. A more or less exact rule is that varying the water content by 0.5% causes the nitrogen percentage of the nitrocellulose to vary by about 0.1–0.2%. The quantity of acid to be used for the nitration of cotton or wood pulp cellulose is chosen so as to make it possible to saturate the cellulosic material with acid quickly and uniformly. The composition of the mixture changes during nitration owing to the consumption of nitric acid and the production of water during the reaction. Hence a large excess of acid should be used, so that the change in its

composition is negligible during nitration and hence a more uniform nitration is achieved. The use of a large excess of acid also makes it possible to use a less concentrated acid, as the dilution during nitration is relatively less.

The ratio of cellulose to acid used in practice ranges from 1:40 to 1:60, and in exceptional cases may be 1:80. A larger excess of acid is also recommended for nitrating poor quality material, which is much more difficult to wet with mixed acid.

The cellulose to acid ratio also depends on the method of nitration. Thus if nitrators equipped with mechanical stirrers are used, the nitration proceeds quietly and evenly so that a smaller excess of acid can be used.

The exact composition of mixed acids and the cellulose to acid ratios are included in the detailed descriptions of particular methods of nitration.

Economy in the consumption of acid in a nitrocellulose plant is achieved by fortifying the spent acid with concentrated nitric acid, sulphuric acid and oleum (see Vol. I) for further use.

The loss of acids is due mainly to the ability of nitrocellulose to retain a considerable amount of waste acid after being centrifuged. It has been established that 100 kg of nitrocotton retain as much as 100 up to 150 kg of acid. In addition, there is some loss in handling, and a further loss of acid vapours, mainly those of nitric acid, carried away by the ventilation air.

NITRATION IN POTS

The oldest method of nitrating cotton consisted simply in immersion in acid. The cotton was allowed to remain for a certain time in the acid and then the combined charge of a dozen pots was transferred to a centrifuge to separate the nitrocotton.

An improvement to the pot method was introduced by Abel. It consisted in dividing the process of nitration into two operations. First the cotton was immersed for a short time in a very large volume of acid. Then it was removed and transferred to pots in which the cotton was nitrated slowly by the acid taken up in the first operation.

About 200 kg of nitrating acid mixed in the ratio indicated in Table 93 are used for each charge.

The temperature of the acid at the beginning of the process lies within 20 and 25°C, and as the nitration proceeds, it may rise to 30, or even 35°C if there is no cooling. 800–900 g of cotton are introduced rapidly into the vessel containing acid, and pressed down to the bottom. To facilitate this operation, the cotton is held with tongs. It is removed after some 5–6 min. Subsequently it is laid on the net attached to the upper edge of the pot and the excess of acid is pressed out of the cotton (which is already nitrated to some extent), by means of an aluminium spade operated by a handle (Fig. 135). The cotton still contains 9–12 times its weight

TABLE 93

THE POT PROCESS FOR PRODUCING GUNCOTTON

Type of nitrocellulose	Composition of the acid	HNO_3	H_2SO_4	H_2O	NO_2
CP_1	mixed acid	15.5	72.5	11.5	0.45
	spent acid	12.3	74.2	13.0	0.48
CP_2	mixed acid	16.5	65.5	17.5	0.50
	spent acid	14.3	66.5	18.5	0.70

of acid after pressing. It is transferred into the covered stoneware or aluminium pot standing nearby, and a series composed of several pots is transported on a truck to concrete basins, to be cooled with running water (Fig. 136).

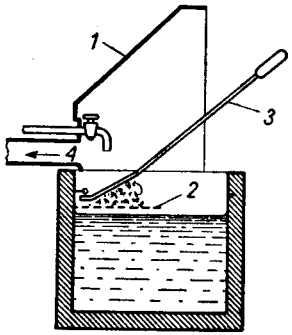

FIG. 135. Nitration pot according to Abel (no cooling jacket is shown): *1*—fume hood, *2*—net, *3*—aluminium spade with a handle, *4*—ventilation pipe.

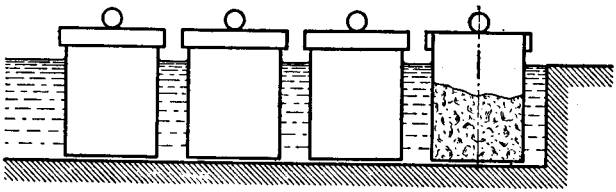

FIG. 136. Nitrating pots for "ripening" of nitrocellulose.

Here the nitrocotton ripens for the following period:

CP_1 for 6–10 hr
CP_2 for 3– 4 hr

Spontaneous decomposition of the nitrocotton may occur during the process of ripening, provoked by a variety of causes, e.g. the entrance of water into the pots due to careless handling or to a defect in the pot itself, such as a crack, or the

use of too warm cooling water in the summer, which permits the temperature in the pot to rise.

After the ripening is finished the contents of a dozen up to twenty pots, i.e. about 25 kg of guncotton, are transferred to a centrifuge to extract the excess of acid. The content of acid is reduced in this way to some 100–150%. Safety precautions during centrifugating and the removal of the centrifuged guncotton are described later.

After the cotton has been removed from the nitration tank (Fig. 135) the composition of the acid in the tank is adjusted so that in quantity and strength of it remains unchanged throughout. The waste acid from the centrifuge is low in nitric acid. The regeneration of this spent acid by addition of oleum and fresh nitric acid is uneconomic. Spent acid is denitrated.

According to French data the consumption of raw materials in the production of 100 kg of guncotton CP_1 (coton-poudre No 1) is as follows:

cotton	63 kg
nitric acid	126 kg
sulphuric acid	123 kg

From 100 parts of cotton, 159 parts of guncotton are obtained. The consumption of raw materials for the manufacture of lower nitrated (CP_2) nitrocotton is less economic.

The pot process of nitration is very simple, no elaborate plant is required, and it can be used for nitrating low grade cotton. Because of the long nitration time it is possible to make use of nitrating mixtures containing little nitric acid, thus reducing the hazards involved in nitration and centrifugation.

A disadvantage of this method is that it involves handling small amounts of raw material, and therefore labour requirements are high. The output per worker per 8-hour shift is only 40 kg of guncotton. The unhealthy working conditions are a serious drawback; the atmosphere is contaminated by nitrous fumes, which escape because the reaction vessels are not tightly closed.

Although the pot process should be considered as obsolete and not competitive with more modern mechanical nitrators, it may still be considered as an auxiliary method, useful when it is necessary to organize production quickly and for a low outlay or when cellulose of low grade must be nitrated.

The pot process was widely used in Russia, France and Great Britain, during World War I.

CENTRIFUGAL NITRATION

For a long time nitration of cellulose in a centrifuge was the commonest method used in all countries. The process developed as a result of the centrifuge constructed by Selwig and Lange [13] that produced considerable amounts of nitrocellulose from one charge during a relatively short time.

The centrifuge shown in Figs. 137 and 138 is the principal unit of the plant.

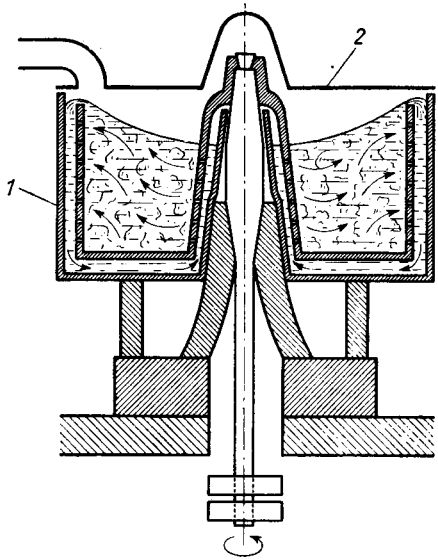

FIG. 137. Diagram of a nitration centrifuge of Selwig and Lange, according to Pascal [14].

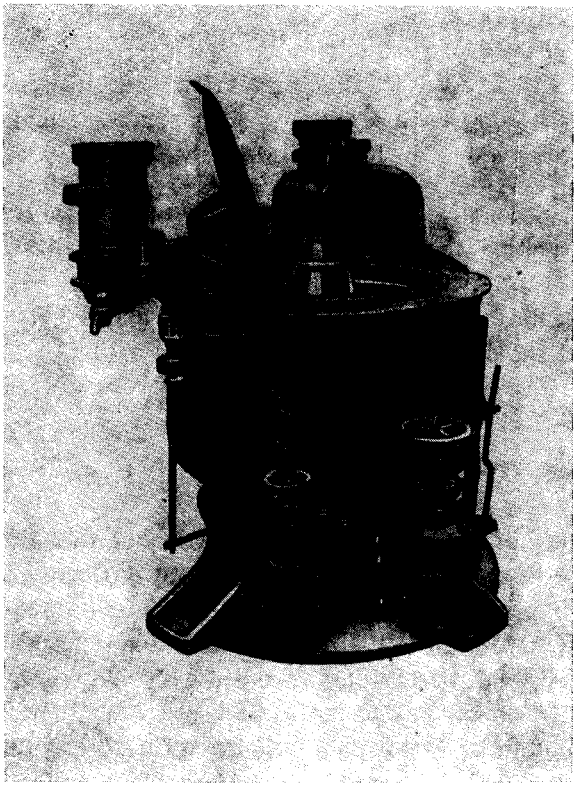

FIG. 138. Nitration centrifuge of Selwig and Lange [13].

The nitration centrifuge is a cylindrical steel vessel (*1*), 0.55–0.65 m high and 1.1–1.3 m dia., suspended on a fixed support erected on a strong foundation. Inside the vessel there is a basket of stainless steel sheet with 5 mm perforations, mounted on a rotating vertical shaft. It is made in various sizes: diameter 1.0 m, height 0.4 m (small model) or diameter 1.2 m, height 5.5 m (large model). An important constructional detail of steel vessel (*1*) is the protection of the shaft against corrosion by the nitrating acid. The shaft can run at both high and low speeds. The whole is closed at the top by an aluminium cover (*2*), equipped whith an exhaust duct through which acid vapours are removed. Acid is fed in and removed through a pipe in the bottom of the vessel (not shown in the sectional view) which is branched to connect with: (a) the metering tank for the mixed acid (inflow), (b) the spent acid tank (outflow).

The process of nitration is carried out as follows: according to the size of centrifuge, either 600–650 kg or 1000–1200 kg of nitrating acid mixed in the ratio given in Table 94 are introduced into the centrifuge.

TABLE 94

THE CENTRIFUGAL NITRATION PROCESS OF GUNCOTTON MANUFACTURE IN FRANCE [14]

Type of nitrocellulose	Composition of the acids	HNO_3	H_2SO_4	H_2O	NO_2	Specific gravity (at 15°C)
CP_1	mixed acid	21.25	66.25	120	0.50	1.738
	spent acid	18.75	67.50	13.2	0.55	1.734
CP_2	mixed acid	20.00	61.75	17.5	0.75	1.694
	spent acid	17.30	63.30	18.6	0.80	1.692

In the manufacture of high nitrogen guncotton (13.45% N) a more concentrated mixed acid should be used, composed of:

HNO_3	22.1%
H_2SO_4	68.4%
H_2O	8.5%
NO_2	0.5%

The temperature of the acid for the production of this nitrocellulose should be 20–30°C, while in the production of lower nitrated guncotton (CP_2) a temperature of 25–33°C is permitted. The acid is maintained at the required temperature in special tanks (temperature stabilizers) situated above the metering tanks. The stabilizers are heated with warm water or cooled with cold water, usually by means of a coil.

A charge of cotton or wood pulp cellulose of 11–15 kg for a small unit or 20–22 kg for a large one is immersed in the acid so that it is rapidly and evenly distributed in the basket.

This task is carried out by means of a special aluminium or aluminium tipped steel fork. Local overheating followed by decomposition of the nitrocellulose can occur at the boundary of the acid-wet and dry substance, if immersion is not uniform. This danger is particularly liable to occur with insufficiently purified cellulose, which does not readily take up the mixed acid.

The cotton to acid ratio should lie within the limits 1:40 to 1:60. The most widely used range is 1:50 to 1:55.

After the centrifuge is loaded it is shut, and put in motion at about 20–25 r.p.m. for a period of 20–45 min.

The rotatory movement forces the acid to circulate through the appertures in the basket into the fixed outer case whence it flows down, below the basket towards the shaft and so back into the basket again. Due to the circulation of acid uniform and rapid nitration is achieved.

It has been demonstrated experimentally that the maximum nitrogen content of the product is attainable in this process yet within 15–20 min. For the time of nitrating cotton in a centrifuge at 25°C, Pascal [14] reports the figures listed in Table 95.

TABLE 95

THE TIME OF NITRATING COTTON IN A CENTRIFUGE (AFTER PASCAL)

Time min	Nitrogen content in CP_1 %	Amount of unnitrated substance %	Nitrogen content in CP_2 %	Amount of unnitrated substance %
5	11.75	5	10.95	10
10	12.93	—	11.30	—
15	13.10	—	11.65	—
20	13.10	—	11.95	—
25	13.10	—	—	—

After nitration is finished, the centrifuge is run at high speed (1000–1100 r.p.m. for the smaller centrifuge or 600–800 r.p.m. for the larger unit), in order to separate the nitrocotton from the spent acid. The nitrocellulose obtained still contains 100–150% of spent acid. After 5–7 minutes' centrifuging, the nitrocellulose is removed by means of aluminium forks, as illustrated in Fig. 139.

During nitration nitrocellulose occasionally catches fire. It has now been made clear that these accidents are caused mainly by the nitrocellulose's greater absorptive power for HNO_3 than for H_2SO_4 from the spent acid (p. 327). As the result, the composition of the absorbed acid differs from that of the liquid phase and corresponds to a higher degree of nitration. The acid retained by the nitrocellulose causes secondary nitration during centrifuging, a phenomenon which is accompanied by the development of a certain amount of heat. Towards the end of nitration, there is

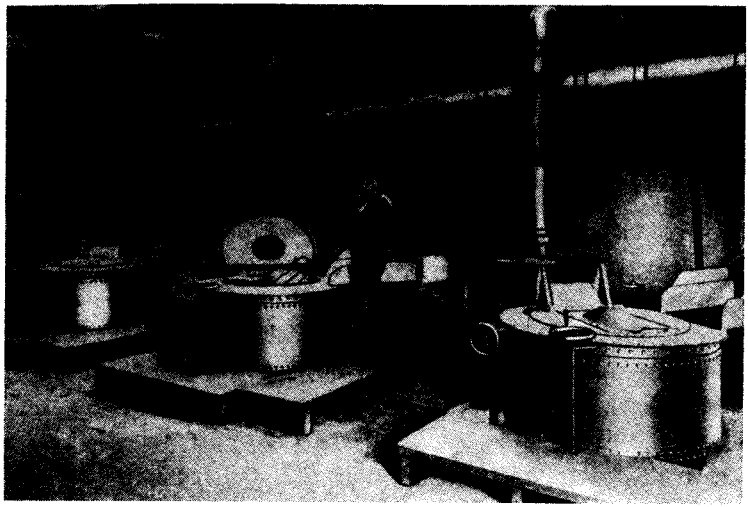

FIG. 139. General view of nitration centrifuges. Discharge of nitrocellulose with aluminium forks (Bofors Nobelkrut, Sweden).

no large volume of acid left to play the part of a thermostatic liquid. Hence the temperature of the product may rise sufficiently to provoke self-ignition. Spontaneous ignition of this kind is particularly frequent while manufacturing higher nitrated guncotton during the summer. Insufficiently purified cotton or wood cellulose catches fire more easily than a pure material owing to decomposition of the impurities or to uneven nitration.

Other stimuli can also cause nitrocellulose to ignite: a drop of lubricant, or a drop of water falling upon the centrifuged nitrocotton, e.g. off the wet fork, may cause a fire, rapid decomposition or even explosion.

Further, too much haste to unload the product by means of the fork, before the centrifuge has stopped, may bring about an explosion, due to the friction between the fork and the inner surface of the moving basket. The use of a steel fork is particularly dangerous and has caused many accidents.

If the decomposition is not of a rapid character, then it can be controlled by immediately pouring cool acid into the centrifuge.

As a precaution should fire occur, the workers should be provided either with protective helmets, equipped with a fresh air supply, or with masks and absorbers, and they should also wear protective clothing of asbestos or thick wool. If a violent fire occurs, the building must be evacuated, since to remain in an atmosphere containing a high concentration of nitrogen dioxide, even for a short time, is very dangerous. This is discussed in more detail on p. 407.

The centrifugal nitration process is reasonably economic. However, it requires well instructed personnel, it is troublesome for the workmen, and its electric power requirements are high.

For each centrifuge, two workers are required, and the rated output per hour of the smaller type centrifuge is 35 kg of nitrocellulose, but taking into account

delays and minor repairs, the average hourly output rarely exceeds 30 kg of nitrocellulose, i.e. 120 kg of guncotton per man per 8-hour shift.

According to French calculations dating from World War I, the consumption of raw materials and the power requirements per 100 kg of guncotton produced was:

cotton	61 kg
HNO_3	140 kg
H_2SO_4	81 kg
electric power	6.5 kWh

During World War I attempts were made to recover the absorbed nitric acid from the guncotton after centrifuging, by washing with sulphuric acid. No satisfactory results were attained, however as the sulphuric acid failed to penetrate deeply into the closely packed layer of nitrocellulose, and the quantity of recovered nitric acid was insufficient to cover the cost of the operation.

However, during World War II a method of recovering nitric acid by washing the nitrocellulose in the centrifuge was taken out in Germany, covering the use of spent acid, as will be discussed later (see p. 390).

After being spun in the centrifuge the nitrocellulose is transported via a stoneware channel to a neighbouring shop, in which the preliminary stabilizing operations, i.e. water washing, is carried out.

Usually two centrifuges are connected to a common channel, as shown in Fig. 140.

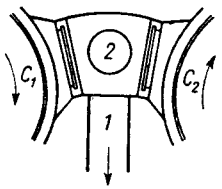

FIG. 140. Diagram showing two centrifuges combined with a drowning trough: C_1 and C_2—two centrifuges, *1*—ventilation pipe, *2*—syphon, according to Pascal [14].

The channel comprises a stoneware funnel, having a collar through which a powerful stream of water enters from different sides, and a stoneware pipe with a U-bend to form a siphon, sketched in Figs. 141 and 142. The diameter of the pipe should be at least 30 cm. Above the funnel there is a hood connected with the fume ducting system. Nitrocellulose is carried by the water flowing down the channel, and thus transported to the next building.

It is extremely important to supply the runway with an abundant quantity of water when the nitrocellulose is introduced. Explosion may occur if nitrocellulose is unloaded from the cetrifuge to the trough while the latter is empty due to an oversight by the worker, or to an interruption in the water inflow. The explosion is caused by the contact between the acid nitrocellulose and the small amount of water remaining in the channel after the preceding load was emptied.

In order to avoid such dangerous errors, automatic safety devices may be incorporated, so that for instance, the cover of the channel cannot be opened unless a full stream of water is flowing through it.

The consumption of water is large, amounting to some 120–150 l. per 1 kg of guncotton.

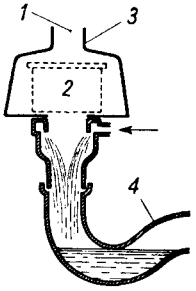

FIG. 141. Diagram of the drowning trough: *1*—ventilation pipe, *2*—aperture to discharge nitrocellulose, *3*—fume hood, *4*—syphon, according to Pascal [14].

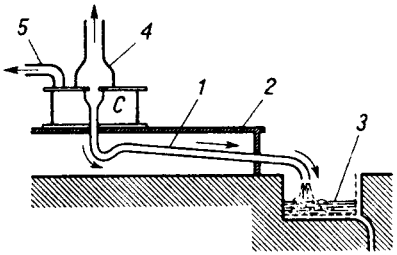

FIG. 142. Diagram of the connection of a centrifuge (*C*) with a drowning trough: *1*—syphon, *2*—service platform, *3*—trough, *4, 5*—ventilation pipes, according to Pascal [14].

THOMSONS' METHOD

The process patented by the Thomsons in 1903 (J. M. Thomson and W. T. Thomson [15]) was used only in Great Britain, though during World War I it was used to a lesser extent also in France. It has now been superceded by the use of nitrators with mechanical stirring.

The principle features of Thomsons' method are: (*1*) immersing the cotton in the acid, and (2) after nitration washing out the acid with water.

The nitrator sketched in Fig. 143 is a cylindrical stoneware vessel of internal diameter 1.1 m and depth 0.4 m, strengthened with an iron belt. Its conical bottom is fitted with an outlet pipe. A three-way valve is provided for evacuating and filling the vessel with acid. Inside the vessel there is a perforated stoneware plate to support the cotton charge. Twenty five to twenty nine centimeters above this plate supports carry a perforated aluminium plate 15 mm thick, which acts as a false

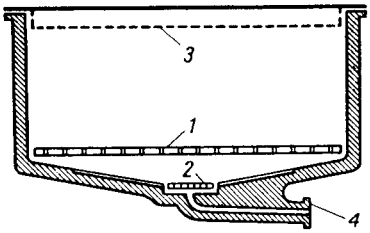

FIG. 143. Diagram of Thomsons' nitrator: *1*—perforated bottom plate of stoneware, *2*—filtering stoneware plate, *3*—perforated aluminium plate, *4*—discharge pipe, according to Pascal [14].

bottom. The nitrator is covered with an aluminium hood connected to the fume duct. The units are grouped in batteries of four nitrators.

Nitration in the Thomsons' plant is carried out as follows. Some 500–540 kg of nitrating acid mixed in the ratio reported in Table 96 are introduced

TABLE 96

THE NITRATION OF COTTON BY THE THOMSONS' METHOD, AS APPLIED IN FRANCE [14]

Type of nitrocellulose	Composition of the acids	%			
		HNO_3	H_2SO_4	H_2O	NO_2
CP_1	mixed acid	21.5	69.75	8.55	0.25
	spent acid	18.2	71.0	10.5	0.30

from beneath into the vessel.

The nitration is performed without stirring, and hence with a more concentrated nitric acid than in the centrifugal method, so that the process proceeds more rapidly. The temperature of the acid is 24–25°C. A charge of 14–18 kg of cotton is immersed in the acid so that it is spread uniformly throughout the vessel. The proportion of cotton to acid varies within the range 1:30 to 1:38.

When the cotton has been introduced, the aluminium plate is placed in a position such that the meniscus of acid lies halfway up the perforations (Fig. 144).

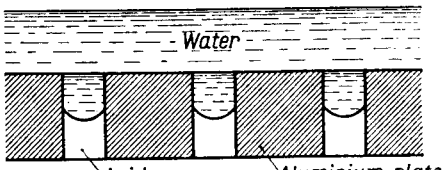

FIG. 144. Diagram of hydraulic closure of a Thomsons' nitrator.

Water is then led in carefully by means of a rubber pipe lying on the aluminium plate so as to form a hydraulic seal, i.e. the water in contact with the acid in the plate

perforation creates two layers of liquid immiscible owing to the difference in their specific gravities. Moreover, the small diameter of the perforations makes mixing of the two liquids difficult.

Due to this water seal, acid vapours do not escape from the nitrator, and the atmosphere in the nitration shop is unpolluted. After the nitrator is loaded the ventilation hood is removed to a neighbouring vessel which is then charged in exactly the same way.

The nitration process lasts $1\frac{1}{2}$–2 hr for the manufacture of high nitrated guncotton. For the production of lower nitrated guncotton 1–$1\frac{1}{2}$ hr is long enough.

After nitration is finished the apparatus is slowly emptied at the rate of about 150 l. of acid per hour. At the same time cold water supplied by a rubber pipe is allowed to flow at the same rate onto the surface of the aluminium plate so as to maintain the same level of liquid in the nitrator. During this operation acid is displaced by water that also mixes with the acid retained in the guncotton. The boundary between the two liquids falls in the vessel at a rate of 2.5 mm/min.

Smoothness of the displacement and dilution of the acid by water depends to a large extent on the quality of cotton used; only the best grade of cotton is suitable for this system of nitration.

The admixture of water with the acid remaining in the guncotton is accompanied by the development of an appreciable quantity of heat. Water used for this purpose should therefore be cooled at least to 4–8°C in order to prevent the temperature rising above the permitted limit, which would otherwise cause decomposition. In spite of this precaution, on mixing with the acid retained by the nitrocotton, a partial denitration always takes place, so the highest nitrated guncotton cannot be obtained by the Thomson process.

Unstable esters formed during nitrating also undergo decomposition, when water is added. Nitrocotton prepared by Thomsons' method is therefore more stable than the product obtained by other methods. Due to partial denitration, the solubility of the guncotton in an ether–alcohol solution is increased.

Sometimes, e.g. when low-grade cotton is used, sudden evolution of heat and rapid denitration is unavoidable, and simultaneous decomposition followed by inflammation of the guncotton can take place, causing the stoneware vessel to break.

The acid flowing out of the nitrating vessel gradually changes its strength and composition. At the beginning, for $1\frac{1}{2}$ hr, about 250 l. of concentrated spent acid flows out. Its average composition is given in Table 96.

This concentrated spent acid is collected separately, and within the next 15–20 min a further 50 l. of diluted acid is collected. Thereafter acid wash-water flows out, and is neutralized before being allowed to escape to the drains.

The composition of the spent acid varies, as shown in the graph (Fig. 145). At first it contains a relatively small proportion of nitric acid, the HNO_3:H_2SO_4 ratio being 0.24, since nitrocotton absorbs more nitric acid than sulphuric acid. This HNO_3:H_2SO_4 ratio increases significantly when acid partially diluted by water

begins to flow out, because nitric acid absorbed and retained in the guncotton is now washed out with water. After about an hour, the ratio of nitric to sulphuric acid is approximately 0.8.

Concentrate ($d = 1.766$) and dilute acid ($d = 1.16$) are collected in separate tanks, and the acid wash water goes to a neutralizing basin. After washing, the water supply is turned off, and the nitrocellulose is conveyed in trucks to the stabilization house.

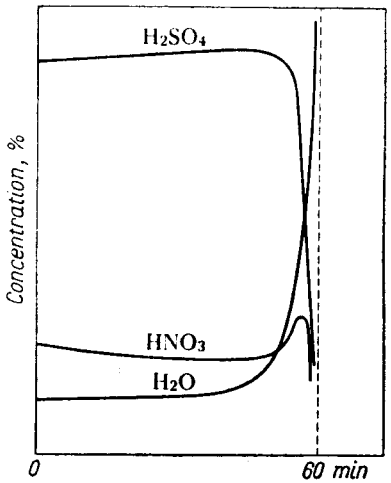

FIG. 145. Change of composition of acid flowing from a Thomsons' nitrator, according to Pascal [14].

Thomsons' process is advantageous for many reasons: the actual operation is simple and the atmosphere in the nitration shops is free from health hazards. The nitrocotton removed from the nitrators contains only a small quantities of acid, and is easier to stabilize than nitrocellulose produced by other methods. The loss of acid is negligible indeed, and this is the chief advantage of the process.

The drawbacks of the method lie in the necessity of using high grade cotton, in the difficulty of achieving a high nitrogen value, and in the need for preparing well-cooled water.

The raw materials consumed in the manufacture of 100 kg of guncotton accordingly to French reports from World War I [14] are:

cotton	58 kg
HNO_3	106 kg
H_2SO_4	84 kg

thus from 100 kg of cotton 172.5 kg of nitrocellulose are manufactured.

From each nitration lasting 4 hr, 22.4 kg of CP_1 were produced corresponding to a daily output of 134 kg in all. The same French sources report that 22 nitrators, served by an 8 man crew, produced 115 kg of product per worker during an 8-hour shift.

NITRATION WITH MECHANICAL STIRRING

Nitrating in vessels equipped with mechanical stirrers is now the most widely used method. It was first introduced by du Pont de Nemours in U.S.A. It was described in 1922 [16].

A nitration unit is composed of four nitrators (Figs. 146–149) constructed of acid resistant steel. Each nitrator (Figs. 146) is fitted with two stirrers that rotate

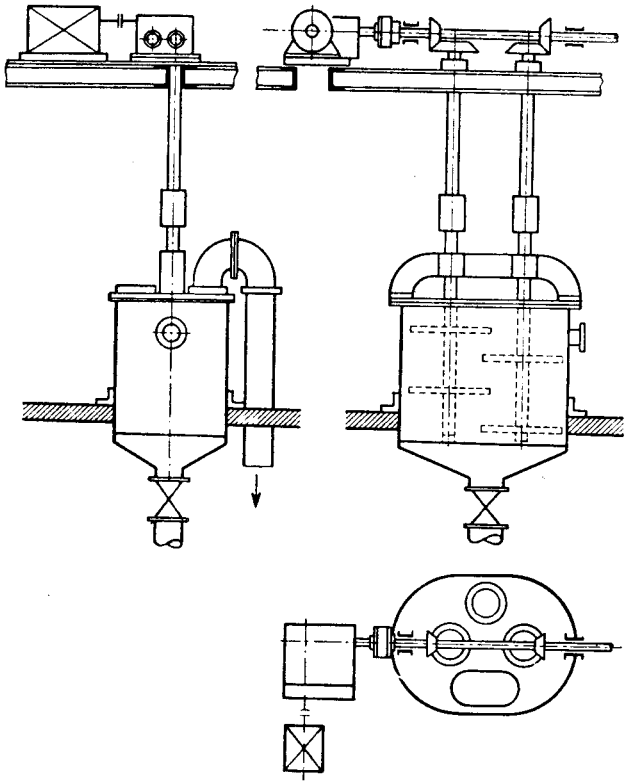

FIG. 146. Diagram of mechanical nitrators (according to Bonwitt [17]).

at about 45 r.p.m. either in the same or in opposite directions. A centrifuge installed below each nitrator receives the contents of the nitrator and separates the nitrocotton from the spent acid. The centrifuge is constructed in such a way that lifting a cone in the centre of the movable basket opens the discharge outlet for the acid allowing it to flow down into a gutter in the storey below. Nitrocotton from this gutter enters a washing tank where the product is freed from acid, and is then sent to the stabilizers. The complete installation is illustrated in Fig. 148.

The process of nitration is as follows: The nitrator is charged with 750 kg of mixed acid of the composition shown in Table 97.

Then 17 kg of cellulosic material are loaded into the nitrator, with the stirrers

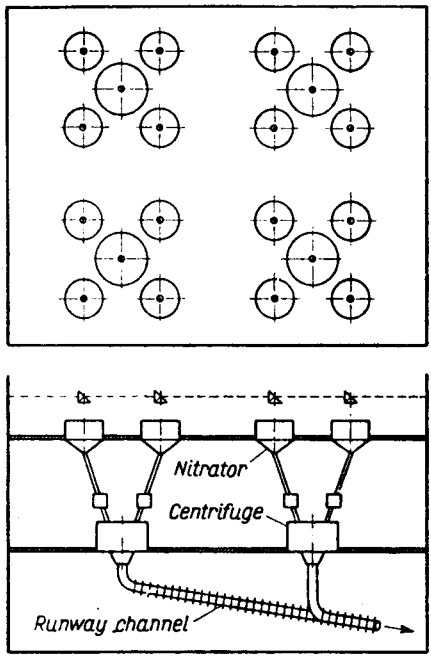

FIG. 147. A plant of four batteries of four nitrators with one centrifuge each (according to Bonwitt [17]).

TABLE 97

THE NITRATION OF COTTON WITH MECHANICAL STIRRING

Composition of the mixed acid, % / Type of nitrocellulose	HNO_3	H_2SO_4	H_2O
Guncotton CP_1	24	66–67	9–10
Collodion cotton CP_2	24	61–62	14–15

running all the time. After 20–25 min the nitration is finished, and the contents of the nitrator are discharged into the centrifuge (Fig. 149).

Centrifugation lasts 5 min, followed by unloading, which takes the same time. In order to maintain continuous operation, the four nitrators are used in turn: while the first nitrator is being loaded with acid and cotton, in the second nitration is just starting, nitration in the third is nearing completion, and the fourth nitrator is being emptied.

Fume ducting connected to the nitrators and to the centrifuge keep the atmosphere in the building pure.

The numerous advantages of the method include absence of complicated operations, low energy requirement, and the fact that it can be used for the nitration

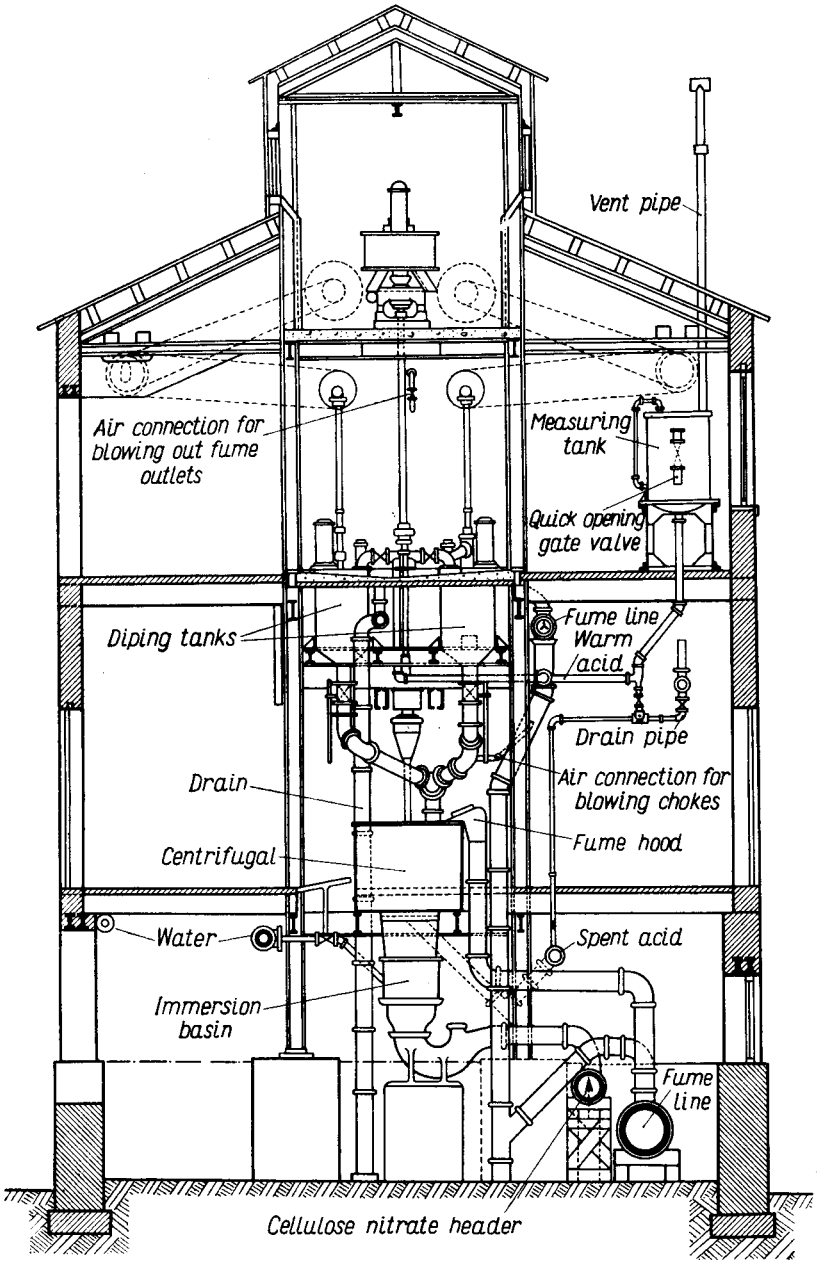

FIG. 148. Diagram of a plant for nitration of cellulose in mechanical nitrators, du Pont system (according to du Pont de Nemours [16]).

of low grades of cotton as well as wood pulp cellulose, from which very uniform products are obtained. The disadvantage of the method is the neccessity for multi-storey buildings.

A modification also exists in which the nitrator is loaded with half the total acid,

FIG. 149. General view of centrifuges in a mechanical nitration plant (Hercules Powder Co., [18]).

the cellulose is then immersed in the acid as quickly as possible and at the same time the remainder of the mixed acid is added.

GERMAN METHOD

The process of nitrating cellulose described below was used in the German factories at Krümmel [19] and Aschau [20] during World War II.

The nitration plant was identical in principle with that described above, with mechanical stirring. In the German method cellulose in the form of crepe paper prepared from 70% birch and 30% spruce was nitrated. Cellulose, torn to pieces in rollers, was dried to reduce its moisture content from 6–7 to 1.2%. Towards the end of the war the drying stage was omitted at Krümmel, and cellulose containing 6–7% of moisture was nitrated, since the time saved and the economy in steam achieved then was reckoned sufficient compensation for the need to make use of more concentrated acids.

The mixed acid was warmed to the required temperature (30°C at Krümmel and 18°C at Aschau) by means of temperature stabilizers. These were cylindrical tanks provided with a coil to heat or to cool the content, and a mechanical stirrer.

The data collected in Table 98 show the composition of the mixed acid used in the German plants. The cellulose to acid ratio was 1:45.

The nitration process consisted in immersing cellulose in the mixed acid. At Krümmel a charge of 25 kg was immersed for 30 min, while at Aschau 21 kg of cellulose were immersed for 40 min. Towards the end of nitration the temperature was around 25°C. The nitrators were provided with stirrers able to revolve at a speed of 200 r.p.m. This rate was maintained during the addition of cellulose to the nitrators, after which the rate of rotation was slowed down to 100 r.p.m. After the nitra-

TABLE 98

NITRATING CELLULOSE BY THE GERMAN METHOD

Composition of the acid, % / Type of nitrocellulose	HNO_3	H_2SO_4	H_2O	NO_2
Krümmel				
Type S: 13.2–13.3% N	22.5	67.5–68.5	9–10	
Type PE: 11.25–11.5% N	20	62–64	16–18	
Aschau				
13.2–13.3% N	22.0	67.8	10.2	2.0
12.4–12.6% N	22.0	62.5	15.5	2.0
11.2–11.5% N	22.0	59.5	18.5	2.0

tion was finished, the contents of the nitrator were let down into the centrifuge, from which separated solid material was removed through the bottom, while the spent acid went to denitration.

At Krümmel, from 100 kg of cellulose 164 kg of high nitrated nitrocellulose (Schiessbaumwolle S) containing 13.2–14.3% of nitrogen and 144 kg of lower nitrated nitrocellulose of 11.2–11.5% N were obtained.

A distinctive feature of the process used at Aschau was the recovery of the acid retained by the nitrocellulose by washing with dilute spent acid in a centrifuge. Three subsequent washings using more and more dilute acid, and finally a water wash, were used.

The composition of the acids used for the successive washings is reported in Table 99.

TABLE 99

COMPOSITION OF SPENT ACIDS USED FOR WASHING NITROCELLULOSE

Washing	Composition of the acids, %		
	HNO_3	H_2SO_4	H_2O
I	18	47	35
II	17	28	55
III	16	14	70
IV	0	0	100

Every acid rinse lasted 30 sec, to be followed by centrifugation for 20 sec. The total washing took 170 sec.

In order to utilize the recovered acids, the liquor from the first washing was sent back to tank I. Half the acid from the second washing was sent to tank I and half to tank II, while half of the third acid rinse went to tank II and half to tank III. The final rinsing water also went into tank III.

The concentration of the dilute acid in the tanks I, II and III, was maintained more or less constant, so that the acid could be used again for washing nitrocellulose. Excess acid went to the denitration plant.

At Aschau the consumption of nitric acid for 100 kg of nitrocellulose of 12.0 to 12.6% N was 90 kg of nitric acid, whereas without the arrangement for recovering the acid, the consumption was 110 kg of HNO_3.

This utilization of the dilute acid produced by washing nitrocellulose is of interest for economic reasons. In former methods the acid wash water had to be neutralized before being discharged to waste. Thus it involved both loss of acid and a large consumption of calcium and sodium carbonate.

While the nitrocellulose was being washed in a centrifuge as described above "fume off and inflame" frequently occurred, generally during the first wash. The accidents were attributed to traces of water remaining in the pipe-line after the final water wash of the preceding charge, for small amounts of water dropped onto a fresh centrifuge charge readily caused it to inflame. One of measures adopted to prevent these ignitions was to push aside the mouth of the water pipe, so as to make it impossible for any water to drop into the centrifuge. A special nozzle was also installed to produce an even spray of acid or water.

Nitric acid recovery included the recovery of the acid vapours from nitrating installations and all tanks, metering tanks and stabilizers holding nitric acid. These vapours were led by means of fume ducts from the nitration plant and by suction pipes from the tanks into towers, where they were sprayed with water or with dilute nitric acid, to produce 50% nitric acid.

CONTINUOUS METHODS OF NITRATION

Numerous methods for continuously nitrating cellulose are to be found in the patent literature. For instance, several patents propose passing cellulose laid on a moving belt through a nitrating bath. The same belt conveys the nitrated cotton to a tank, where it is separated from acid. Subsequently the guncotton produced is unloaded into water. Arrangements of this type were patented [21].

The main drawback of these methods consists in the difficulty of maintaining constant composition of the mixed acid, hence there is liable to be a significant lack of uniformity in the resulting nitration product. A more uniform product can be obtained by using nitric acid vapour [24].

Another method which enables a more homogeneous product to be made by more uniform nitration, was proposed by Juer [22]. The nitrator comprises a rotatory drum inside which is a plate, bent in a spiral form. As the drum turns, this spiral moves the charge in one direction. In a separate pre-nitration vessel provided with a stirrer, cotton and acid are metered and mixed to feed the nitrator batch-wise. The length of the drum and its speed of rotation are arranged so that completely nitrated cotton is delivered. The guncotton produced is separated from the spent acid by conventional methods, e.g. in a centrifuge.

Meissner [23], in a patent for the continuous nitration of cellulose suggests using several U-shaped nitrators coupled together. Cellulose is introduced to one of the nitrators, while another is fed with acid. By means of suitable stirrers it is possible to transfer the contents of one nitrator successively to the following nitrator. Acceptably uniform nitration is achieved by this system.

Up to the present, continuous processes for the cellulose nitration have not been introducted in practice.

New ideas in the manufacture of nitrocellulose consist in nitrating cellulose in the presence of a solvent (e.g. methylenedichloride [25], nitromethane) which is not subjected to nitration but dissolves nitrocellulose and forms a separate phase. The solution of nitrocellulose is then washed with water to stabilize the product. The operations can be made continuous.

Nitrocellulose precipitated from the solution can be subjected to an additional, very brief stabilization (e.g. a 1-hour boil).

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CHAPTER XIV

STABILIZATION OF NITROCELLULOSE

THERE are many methods of stabilizing nitrocellulose. In different countries and in various plants, a variety of techniques are in use, partly as a result of local conditions, e.g. the quality of the water available for stabilization boiling, but influenced also by tradition and by the development of earlier processes.

However, certain fundamental operations are common to all stabilization methods, namely:

(1) Primary washing of nitrocellulose by means of water and boiling in kiers, either in pure water or in dilute acid (the alkaline kiering formerly in use has now been abandoned).
(2) Additional kiering in autoclaves under pressure (in more up to date plants).
(3) Pulping (grinding) nitrocellulose in beaters and in mills respectively.
(4) Poaching (final boiling) in boilers, in water containing alkalis (not always applied).
(5) Certain kinds of collodion cotton for industrial purposes, e.g. for varnishes, celluloid, films, are also subjected to a bleaching process.
(6) Decanting and rinsing the stabilized nitrocellulose.
(7) Removal of mechanical impurities, e.g. sand or long fibres.

Other operations also in use include:

(8) Blending batches of nitrocellulose to form large homogeneous stocks of product.
(9) Centrifuging the nitrocellulose in order to remove excess water.
(10) Semi-hermetic or hermetic packing for transport.

During the various operations enumerated samples are taken to be checked in the laboratory for stability (Abel heat test), degree of fineness, etc.

PRIMARY WASHING AND BOILING IN KIERS

Nitrocellulose delivered from the centrifuges is washed with water either in special vats with stirrers (Fig. 150), or directly in kiers in which the product is then boiled. In the latter case water is introduced into the kier loaded with nitrocellulose and then let out again, the washing being repeated several times.

The drum (*1*) made of perforated plate is equipped with paddles both inside and outside. Nitrocellulose picked up by the outer paddles is thrown over to the neighbouring compartment, while the inner paddles remove water. To the second

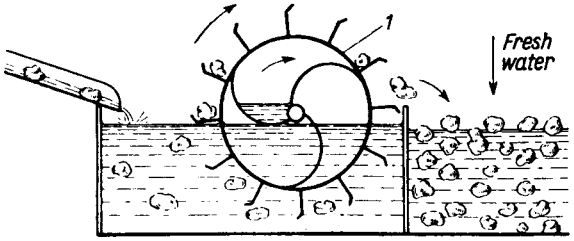

FIG. 150. Diagram of washing nitrocellulose.

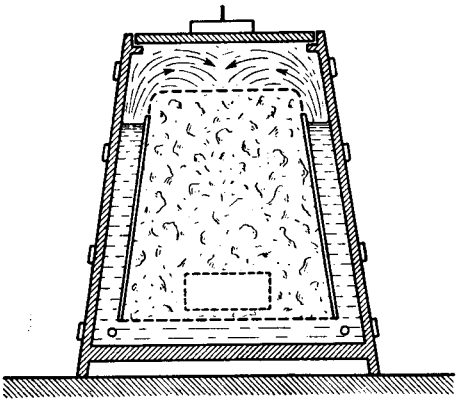

FIG. 151. Diagram of a digester (kier) for stabilizing boiling nitrocellulose, according to Pascal [1].

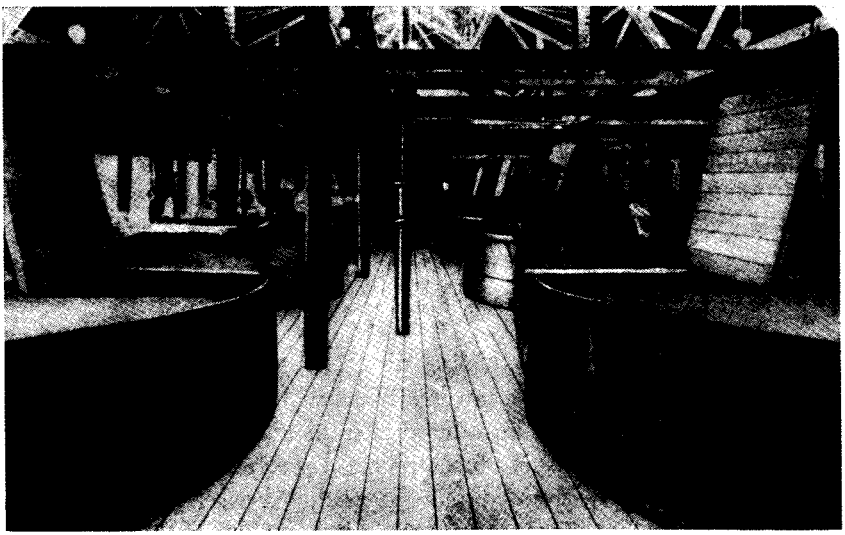

FIG. 152. General view of digesters for stabilization of nitrocellulose (Hercules Powder Co., [3]).

tank fresh water is introduced and a similar drum removes water and transfers nitrocellulose to the next compartment and so on.

The kiers are vats made from wood in the form of a cylinder or truncated cone (Figs. 151 and 152), of 2–50 m^3 capacity (10–20 m^3 is the most common).

Recently, an improvement in construction has been introduced that consists in lining the kiers with stainless steel plates. 100 kg of nitrocellulose is loaded for every 1–2 m^3 of volume of the vat.

The kiers are double-bottomed, the upper "false" bottom being made of perforated acid-resistant sheet or a wood frame lined with perforated stoneware bricks. Live steam at about 3 atm pressure is introduced into the space below the false bottom. In order to ensure a better circulation of hot water and steam in the kier, in many installations boilers are provided with one or more pipes (e.g. four), which are open at both ends and arranged so that the lower opening is situated above the steam inlet. Water and steam rise in the pipes and spout from the top. In this way a vigorous circulation is maintained inside the boiler. An outlet tap is situated in the lower part of the boiler. The kier is loaded with nitrocellulose transported in water, which then flows out leaving the nitrocellulose inside. With this method, which was used in Germany, it is impossible to attain a higher loading density than 50 kg/m^3.

Wet nitrocellulose can be pressed down manually in the kier by workers dressed in protective clothing, rubber shoes and woollen clothing for entering the boiler. In this way, as used in France, the loading density can be increased to 100 kg/m^3.

Although better use is made of the capacity of boiler, the high density of loading has an adverse effect on water circulation, thus making it necessary to prolong the period of stabilization boiling.

Below examples are given of stabilization boiling as carried out in France in CP_1- and CP_2-guncotton manufacture.

The stabilization boiling comprises the following stages:

(a) three water washes, each of 15 min (each wash consists in filling the vat with water, allowing it to remain for 15 min and then removing it);
(b) one 4-hr boil followed by change of water;
(c) one 72-hr boil for CP_1 or one 36-hr boil for CP_2, followed by a change of water;
(d) three boils, each of 1 hr in the presence of calcium carbonate (about 0.5% calculated on the weight of guncotton). Each of the boils is followed by rinsing the load with cold water.

This method of stabilization is very expensive, and takes an exceptionally long time — several days. It is therefore necessary to arrange a considerable number of kiers and hence a large and costly installation is required. Pascal [1] states that in a factory to produce 100 tons of nitrocotton a day some 400–500 vessels of 2–4 m^3 should be installed.

Furthermore, the operation of an installation is also expensive, since 4–5 kg of steam are consumed for every 1 kg of nitrocellulose. A boiler house to supply the kiers with steam should be situated near to the stabilizing house.

The stabilization of guncotton produced by the Thomsons' method is slightly less expensive, as this product is easier to purify. According to Robertson [2] 10 successive boiling and washing operations are to be carried out:

(a) two 10-hr boils.
(b) washing with cold water;
(c) five 4-hr boils;
(d) three 2-hr boils;

The water is changed after each boil. In spite of the relatively short time needed for stabilization, the Thomsons' method is too expensive.

The introduction of autoclaves, which considerably reduced the time required for boiling, brought about a marked improvement in commercial methods of stabilization. The high installation costs for the high pressure system are fully compensated by the very much shorter stabilization process.

In the plant at Krümmel [4] nitrocellulose was boiled with water in kiers of 14 m^3 capacity. S-type was boiled for 6–8 hr, and collodion nitrocellulose (PE-type) for only 3 hr.

In the factory at Aschau [5], boiling was carried out using water acidified with 0.5% of sulphuric acid, the operation lasting up to 10 hr for S-nitrocellulose, or up to 8 hr for PE-nitrocellulose. In both plants, nitrocellulose was then kiered under pressure.

BOILING UNDER PRESSURE (KIERING IN AUTOCLAVES)

According to the stabilization method used in German factories, after primary stabilization in boilers, the nitrocellulose was subjected to a short kiering in autoclaves made from acid-resistant steel with a hot-water circulation (Fig. 153).

At Aschau [5] autoclaves of 5 m^3 capacity were used, loaded with 400 kg nitrocellulose and 4 m^3 of water. The autoclave was equipped with a stirrer, and was heated by means of both direct and external heat, under a pressure of 12 atm until the desired temperature of 140°C was reached, after which the temperature was maintained exclusively by means of external heating. Kiering took about 15 min.

At Krümmel [4] kiering was carried out for 6 min at a temperature of 142–145°C.

After kiering, the contents of the autoclave were transported by means of a pump or in a water conveyer to the beaters, where the fibres were broken down.

Treatment in autoclaves was also used in earlier years to reduce the viscosity of collodion cotton intended for the manufacture of varnishes. For the same purpose, a water slurry of nitrocellulose may be "boiled" under hydrostatic pressure in tubes, as a continuous process. These methods are discussed in detail in the chapter devoted to the manufacture of collodion cotton for varnish production.

According to Miles [7] at Ardeer, rotary autoclaves, spherical in shape, made from stainless steel are used. A pressure of about 3.5 kg/cm^3 and a temperature of *ca.* 142°C are maintained inside the autoclave. The nitrocellulose to water ratio is 1:10, and since the nitrocellulose contains less than 0.25% of acids (as H_2SO_4), the acidity of the water in which the kiering is performed is less than 0.03%.

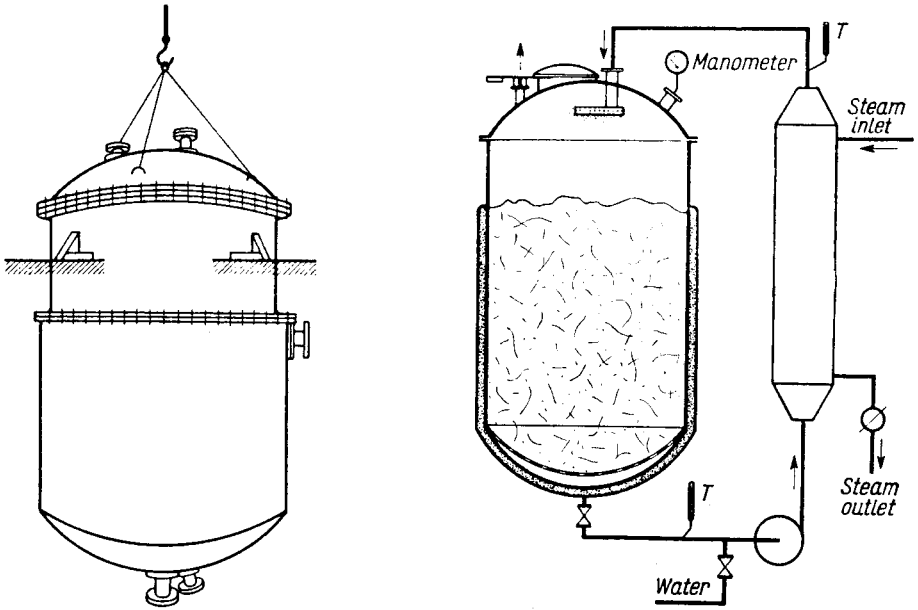

FIG. 153. Autoclave for stabilizing nitrocellulose [6].

During kiering a partial degradation of the nitrocellulose takes place, followed by the dissolution of part of the product. The loss thus caused is higher in the case of lower nitrated cellulose, e.g. 10.8% N, than with higher nitrated products, e.g. containing 12.2% N. On the other hand the denitration is more severe with higher nitrated products. This is most evident in the initial stage of boiling. A phenomenon of this kind was described by Desmaroux [8].

The viscosity of nitrocellulose is also reduced. For instance, during 2 hr kiering nitrocellulose with a polymerization degree P of 200 undergoes a de-polymerization to $P = 50$, at the same time losing 0.12% of nitrogen.

The autoclave is equipped with a device to remove any gases produced during pressure boiling. The composition of the gases evolved varies within the range:

20–50%	CO_2
25–35%	NO_2
10–25%	NO

PULPING

An important operation in the stabilization of nitrocellulose, particularly for materials containing over 11.5% N involves cutting the fibres into short pieces. Only nitrocellulose of low nitrogen content, below 11.5% N (collodion cotton) can be stabilized adequately without such a treatment.

Generally, shortening the fibres is carried out in beaters, equipment adapted from the paper industry. The operation is known as pulping.

The majority of paper beaters are of the type illustrated in Fig. 154, which com-

prises a cast iron tub divided by a vertical partition (*1*). In one half of the tub a cutting drum (*2*) is placed, provided with steel teeth lying parallel to the axis of the drum. As it rotates, the drum meshes with identical fixed teeth (*3*) attached to the bottom of the vessel.

The tub is filled with nitrocellulose and water. The semi-liquid slurry passes between the teeth, where the fibres are cut by the knives (*2*) and (*3*) that function

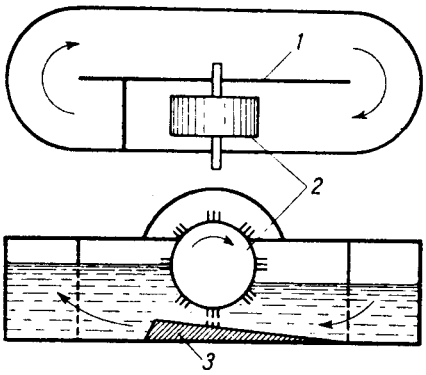

FIG. 154. Diagram of a beater (small size), according to Pascal [1].

like shears. Due to the high speed of rotation of the drum (100–150 r.p.m.), the semi-liquid slurry is drawn between the knives and thrown on to the other side. A considerable slope at the bottom helps to maintain a high velocity. The stream of pulp follows to the second half of the beater whence it returns to the first compartment, to be drawn once more by the revolving drum between the knives, and so on.

At the beginning, the circulation of the slurry is difficult owing to its uneven consistency, so movement of the mass is aided by wooden paddles. Gradually the fibres and lumps of nitrocellulose are cut, the consistency of pulp becomes more and more uniform, and the slurry flows more easily as the nitrocellulose becomes finer. The paddles should however be kept ready to use until the end of pulping, to move the mass by hand should any congestion occur. As pulping proceeds, the bearings that support the shaft of the cutting drum are gradually lowered, so that the distance between the fixed teeth and the drum's knives is gradually reduced.

The time required for pulping depends on the design of the beater and on the type of nitrocellulose. Thus, the more highly nitrated the cellulose, the lower the mechanical strength of fibres, i.e. the more brittle they are and the more easily torn to pieces.

Very large beaters (capacity 25 m^3), may be used (Figs. 155 and 156). Here, the cutting drum is situated at one end of the tub which is made either of cast iron, from a couple of units to be assembled together, or of concrete. Concrete vessel are lined internally with glazed tiles. The trough is divided into two by means of a vertical baffle plate. In these compartments the bottom is inclined in opposite directions in order to facilitate the circulation of the pulp.

The dimensions of the equipment used in France are as follows: length 5.5 m, width 2.4 m, height 1.2 m drum diameter 1.35 m and length 1.75 m. The drum is equipped with 80 knives.

Vessels of these dimensions are loaded with a pulp charge of 1000 kg guncotton. The tub is filled with 15 m^3 of water, and gradually 1000 kg of boiled nitrocotton

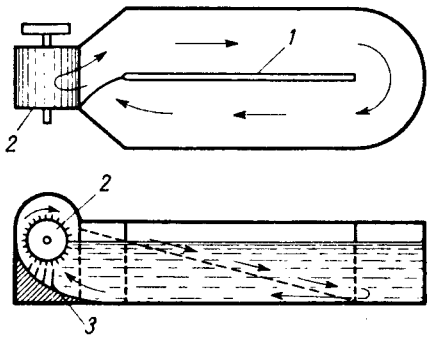

FIG. 155. Diagram of a beater (large size), according to Pascal [1].

FIG. 156. General view of a beater plant (Bofors Nobelkrut, Sweden).

(dry weight), are added during a period of 2 hr. The drum revolves at a rate of 125 r.p.m. During loading, the men move the material with paddles to cause the mass to get under the cutting drum. After the total charge of guncotton has been loaded pulping is continued for 2–4 and 4–6 hr for high and lower nitrated guncotton, respectively.

During the pulping, sodium carbonate or calcium carbonate is added to neutralize the residual acid freed from inside the cut fibres. Initially enough sodium carbonate is added to prepare a solution of about 0.1% of Na_2CO_3 concentration. Later on, during the process, more sodium carbonate is added to keep the pH-value within

the range 7.0–9.0. The admixture of carbonate prevents the acidification of the reaction medium, and protects the cutting knives against corrosion. Calcium carbonate is used in excess so that a certain amount of it remains in the nitrocellulose.

The adjustment of the knives of the cutting drum so as to maintain close contact

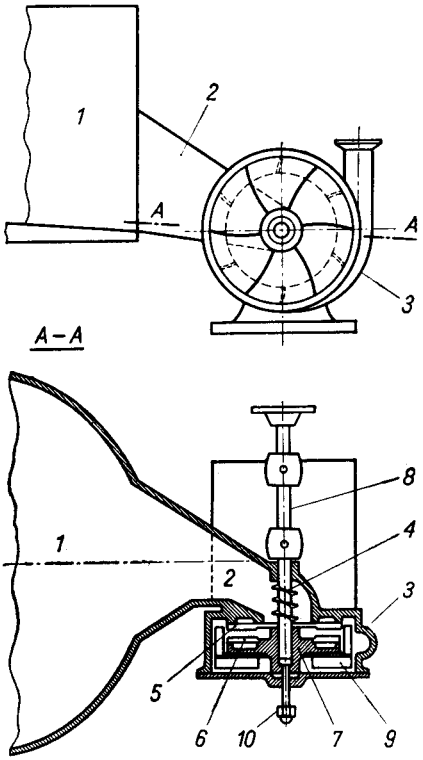

FIG. 157. Disk mills, Raczyński system [9].

is carried out in accordance with the indications of an ammeter. Using a 100 HP motor the consumption of electrical power is 30 kWh per 100 kg nitrocotton.

In the factory at Krümmel [4] beaters of 14.5 m^3 capacity were used, their effective capacity approaching 2400 kg of guncotton. In this machine S-type nitrocellulose was pulped for 5–6 hr, whereas for PE-type nitrocellulose pulping time was extended to 10–12 hr. The fibre length after pulping was 0.2–0.5 mm. The operation was regarded as complete when a specimen taken from the beater demonstrated a fineness characterized by a value of 80–100 cm^3. The test consists in stirring 10 g nitrocellulose with 250 cm^3 of water in a graduated cylinder, the volume occupied by the nitrocellulose being measured after a few hours. Under these conditions a well pulped nitrocellulose occupies a volume less than 140 cm^3 corresponding to a mean fibre length of 1 mm.

Raczyński [9] replaced the beaters for pulping nitrocellulose by disk mills (Fig. 157). A nitrocellulose water suspension flows down from a tank (*1*) through

the channel (*2*) into the mill (*3*). The mill simultaneously acts as a draw-lift pump. By means of the worm (*4*) the suspension is conveyed to the milling disks (*5*) and (*6*). The disk (*5*) is fixed, and the disk (*6*) is attached to the outside of a rotor (*7*) which revolves about the spindle (*8*). The other surface of the rotor (*7*) is equipped with paddles (*9*) which throw the slurry through a vertical outlet during rotation. The screw (*10*) presses the rotor carrying the disk (*6*) into the fixed disk (*5*).

Markiewicz, Zenftman and Raczyński [10] included the Raczyński mills in a pulping plant (Fig. 158) which comprised a battery of eight mills (*1–8*) and two

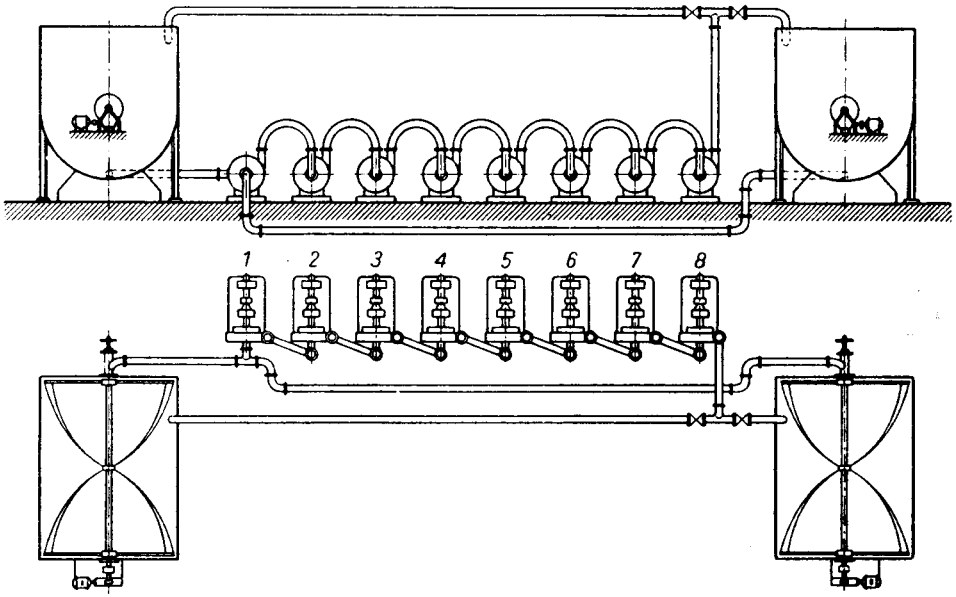

FIG. 158. Diagram of a Raczyński milling plant [10].

tanks in which nitrocellulose was kept in suspension in water by means of stirrers. The suspension from one tank proceeds through the disk mills into the other tank. When the whole contents of one tank have been transferred to the other one, the direction of flow of the slurry is reversed.

The introduction of the Raczyński mill revolutionized the pulping of nitrocellulose fibres. Their most important advantage is that they require only 25–30% of the power needed for beaters. The design of the Raczyński mill has since been improved by Wrocławski [11].

Attempts have also been made to replace the beaters by conical mills in which conical knives on the rotor mesh with fixed knives. Owing to its shape and to the inclination of the knives, the mill also acts as a pump, drawing the suspension of nitrocellulose from the tank and returning it to the same or to another tank. These mills have not been wider adopted in practice, since they have no material advantage over conventional beaters.

After being pulped, the nitrocotton fibres are pumped into the poacher. If the consistency is insufficiently liquid then water is added to the slurry during pumping. The beaters or mills are emptied through a discharge pipe in the base.

A diagram illustrating the layout of a beater or a mill with a poacher, the position of the mixer and the final purification unit, is outlined in Fig. 159.

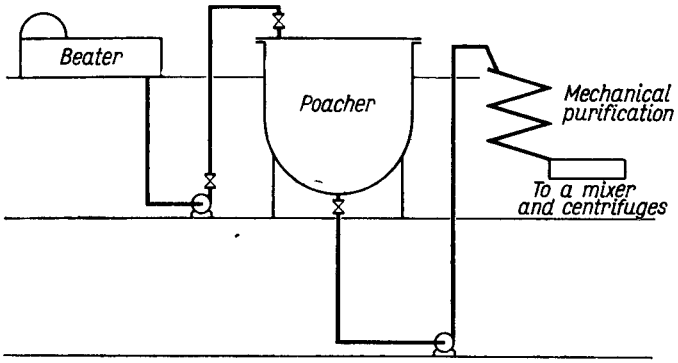

FIG. 159. Diagram of a plant composed of a beater, a poacher and a purifier.

Between the beaters or mills and the boilers, an apparatus for separating long fibre nitrocellulose from the cut fibres is inserted. This is a tank carrying a vertical cylindrical screen drum, with apertures 0.4 mm dia. The drum rotates and the cut fibres pass through the sieve into the drum, whence the contents flows to the boilers. The uncut fibres are caught on the surface of the screen from which they are removed by means of a brass knife and recycled to the beaters.

Alternatively, the uncut fibres can be retained in trough-shaped settlers with baffle-plates. This method is usually used for separating nitrocellulose already completely stabilized, as will be seen in the description that followings.

BOILING IN POACHERS

The suspension of cut nitrocellulose fibres in water is transferred with the help of a pump into a boiler (poacher). This is a vertical (Fig. 160) or horizontal (Fig. 161) cylindrical vessel of 10–20 m^3 capacity, constructed of sheet-metal, equipped with a stirrer and heated by direct steam injection.

In France it is customary to add 1–2% of calcium carbonate to the water in which the pulped nitrocellulose is poached for at least 4 hr. The stability of the resulting nitrocellulose is examined by means of the heat test, and if necessary poaching is repeated. This is carried out by allowing the contents of the boiler to settle for several hours, so that the nitrocellulose sinks to the bottom. The water is then decanted from above the nitrocellulose layer, fresh water and calcium carbonate are added, and the poaching is started again, and continued for 2–4 hr.

This procedure is repeated as often as necessary, using fresh water each time.

The weight of calcium carbonate added is equivalent to 0.1–0.5% that of the nitrocellulose.

With high nitrated guncotton (CP_1) the stabilizing process usually consists of two 4-hr poachings, each boil being followed by decantation, for which an outlet tube ending with a funnel is usually used. The stability of the nitrocellulose is then tested, and one or more further poachings in the presence of calcium carbonate,

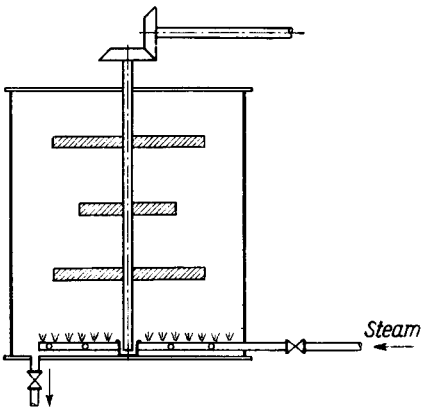

FIG. 160. Vertical boiler (poacher).

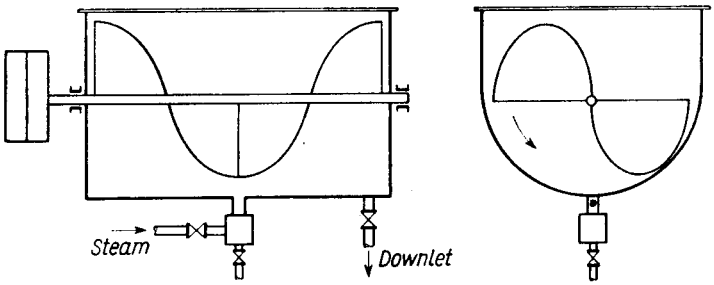

FIG. 161. Horizontal boiler (poacher).

lasting 2 hr, and a couple of water washings are carried out, if necessary. The water washing consists in agitation of the nitrocellulose with cold water, followed by settling and decantation of the water.

In Germany during World War II, cylindrical boilers, provided with mixers, of 10–14 m^3 capacity, were used. The vessels were made of sheet-iron or of concrete lined internally with an acid-resistant material, for instance ceramic plates joined by means of a phenol-formaldehyde resin, "asplit".

In the plant at Krümmel [4] the water suspension of the pulped nitrocellulose of low nitrogen content was stabilized by heating it to boiling point, cooling and refrigerating it, and then washing with water. Nitrocellulose of high nitrogen value, on the other hand, was boiled for several hours until a sample taken from the poacher

passed the standard heat test. Sampling was carried out after 2, 3, 5 and 8 hrs' poaching. Thereafter, if the sample failed to show sufficient stability, the test was repeated every 3 hr.

In the factory at Aschau [5] 13 m^3 boilers were loaded with 1100 kg of pulped nitrocellulose. Nitrocellulose of 11.2–11.6% N was poached for 2–3 hr, whereas nitrocellulose containing 13.2–13.4% N was poached for 5 hr, in water containing 0.25% by weight of sodium carbonate calculated with reference to nitrocellulose.

In Great Britain instead of hot poaching, the pulped nitrocellulose is subjected to repeated washing. This consists in thoroughly stirring the nitrocellulose with water, decanting the water and repeating the procedure with fresh water.

Washing is most usually performed in "washing poachers", rectangular tubs (Fig. 162) divided by a partition into two parts. The slurry of nitrocellulose in water

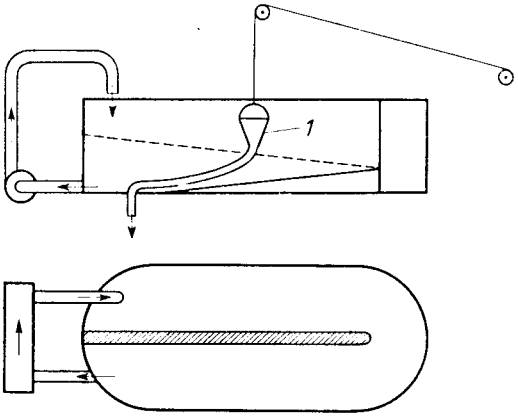

FIG. 162. Washing poacher.

is transferred by a rotary pump from one part of the trough to the other. The bottom of each section of the vessel slopes in opposite direction so as to facilitate circulation. After being stirred with water for some 15–20 min the contents of the vessel are allowed to settle for half an hour, and then the water is decanted from above the nitrocellulose.

Fresh water is then introduced and the stirring is re-started. Washing is repeated at least three times.

In many factories washing of this kind is carried out as a supplementary operation after stabilization of the nitrocellulose by boiling.

BLENDING

In order to produce a homogeneous product, a couple of charges of nitrocellulose are blended after stabilization to make at least 10,000 kg. The mixing is carried out in various types of equipment. For instance large concrete vessels 25 m long, 4 m wide, 2 m high divided by a partition wall into two troughs, and equipped with

a pump to circulate the water suspension of nitrocellulose are used in France. The charge totals 10,000 kg of the material plus 100 m^3 of water (Fig. 163).

In German plants cylindrical concrete tanks equipped with stirrers are the most widely used. The capacity of these tanks is 100 m^3, and they are charged with 10,000 kg of nitrocellulose. After mixing the product for several hours with water,

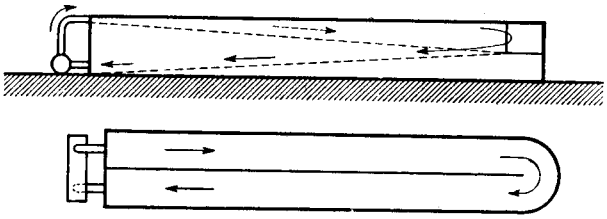

FIG. 163. Mixing tub (according to Pascal [1]).

it is removed through a valve in the bottom of tank and subjected to a final purification.

FINAL PURIFICATION

The final purification stage (screening) removes insufficiently cut fibres, sand, particles of iron and other mechanical impurities picked up by the nitrocellulose during manufacture.

Two types of plants are in use for this purpose. One is a kind of settler, constructed in the form of a sharply inclined, wooden gutter, with a large number of bends. Wooden baffles are placed at intervals along the bottom of the gutter, interspersed with "honeycomb" sections intended to detain sand. After leaving the settler the slurry of nitrocellulose passes through vibrating sieves where the residual uncut fibres are retained. Finally the suspension flows between the poles of an electromagnet which removes iron. Alternatively, the screens for removing long fibres may be situated between the beaters and the poacher, when further screening during final purification is superfluous.

DECANTATION

After the final purification, the suspension of nitrocellulose in water is led into cylindrical decantation tanks, 6–8 m high and 1.5–2.5 m dia. equipped with stirrers. The contents of the tanks are allowed to stand for a time, and then the water is decanted either by means of a funnel (Fig. 163) or through a valve in the side of the tank. The stirrer is then set in motion and the "thickened" pulp of nitrocellulose in water is delivered to a centrifuge.

Most of the water can also be removed from nitrocotton by introducing the pulp into a tank containing a revolving screen drum. The nitrocellulose is retained

on the surface of the screen drum, the water passing through and being removed from the inside of the drum.

DEHYDRATION

The water content of the "thickened" nitrocellulose pulp is reduced to 30–40% in centrifuges of the type similar as those used in the manufacture of sugar. In many plants, additional dehydration is carried out in hydraulic presses, in which the nitrocellulose is subjected to a pressure of about 20 kg/cm^2 and formed into blocks or "cakes" in which the water content is 20–30%. Clearly this is advantageous from the point of view of transport.

The dehydration and pressing of nitrocellulose is often combined with an additional blending. Thus, for example, after centrifuging, the nitrocellulose is placed in a large wooden box in horizontal layers, from which vertical slices are then removed for pressing.

PACKAGING AND TRANSPORTING

Wet nitrocellulose containing 20–40% of water is packed in galvanized iron drums or in semi-hermetic wooden boxes lined with zinc sheet or sometimes only with paraffin wax paper. Rubber gaskets are fitted under the lids. The box lids are fastened down by means of brass screws. Nitrocellulose packaged in this way is accepted for railway transport in separate waggons.

DRAIN WATER

Prior to being discharged to waste, water acidified during the stabilization of nitrocellulose should be neutralized by means of calcium carbonate. Further, all wash-water should be freed from particles of nitrocotton. This is usually accomplished in large settling tanks in the form of divergent cones. Waste water is introduced into the tank at a point roughly half way up. The velocity of water flow is therefore reduced as its level rises, so that the nitrocellulose sinks to the bottom, while water freed from nitrocotton overflows and is discharged. From time to time nitrocellulose (strongly contaminated as a rule) is removed from the bottom of settlers and is destroyed either by means of boiling with milk of lime or by careful burning.

SAFETY IN A NITROCELLULOSE PLANT

Danger exists in nitrocellulose plants even during the first stage of the manufacturing process, while shredding and drying the cellulosic material. Too high a temperature in the drier or contamination of the cotton with lubricating oils are sufficient to cause it to catch fire. Under the influence of a discharge of static electricity, cotton dust present in the air may to explode. Therefore the electric installation must be designed and built with particular care.

Another danger point in nitrocellulose manufacture lies in the nitrating arrangements, particularly in centrifugal nitration processes. If low-grade nitrocellulose catches fire in the centrifuge, sometimes its rate of burning is slow enough to permit the fire to be extinguished quickly, by introducing cool nitration mixture into the centrifuge. The burning of high-nitrated nitrocellulose, on the other hand, is extremely violent, and is difficult or impossible to check and it may pass into explosion (see p. 316).

In the event of inflammation of the centrifuge charge all employers should leave the building immediately, since large volumes of nitrogen tetroxide are evolved, and the atmosphere becomes poisonous. Alyavdin [14] reports that nitrogen tetroxide in air becomes toxic at a concentration of 0.15 mg/l. The inhalation of nitrogen tetroxide at this concentration causes inflammation of the upper respiratory tract and prolonged contact produces inflammation of the lungs. According to the U.S.S.R. industrial health standards (NSP 101–51) the permissible concentration is 0.005 mg/l., a quantity undetectable by smell, since the limiting concentration capable of detection by smell is 0.02 mg/l. (Lazarev [15]).

In a paper by Valada [16] the lethal dose of NO_2 in the air (DL_{50}) in experimental animals was estimated at 1 g/m^3 i.e. 1 mg/l., when breathed for half an hour. According to that author, the symptoms of poisoning are emphysema of the lungs, and the presence of iron pigments in the liver, kidneys and spleen, all indicative of severe globulosis. Should accidental poisoning with nitrogen dioxide occur, the patient should be taken out into the fresh air immediately. In severe cases, oxygen can be administered to relieve the respiration, and intravenous injection of glucose and calcium chloride should be given. In addition the action of heart should be sustained by means of caffeine, camphor or heart glucosides.

Undue haste in unloading centrifuges with forks made of acid-resistant metal, even if it is soft like aluminium, is also dangerous. Explosion of the centrifuge charge have been reported due to attempting to unload the basket before the centrifuge was stationary: friction between the forks and the inside of the basket caused an explosion to occur. It should also be kept in mind that nitrocellulose wet or damp with spent acid is especially liable to decompose. The higher the nitrogen content, the more dangerous it is to handle. Numerous accidents have been caused by touching acid guncotton with wet forks or by allowing water to drip into it (see p. 380).

The later stages of nitrocellulose production are considered less hazardous since the nitrocotton is handled in suspension in water. It is important to prevent the nitrocellulose from becoming dry. Particular attention should be paid to washing down of the clinker bricks or asphalt floor regularly with water.

In the building where stabilization and the final purification of nitrocellulose are carried out meticulous cleanness must be observed. The workmen should wear shoes with rubber or wooden soles, and this footwear must be kept in special boxes or on shelves situated in the rooms in which it is to be worn. It is forbidden to walk outside these rooms while wearing the special footwear so that neither sand nor mud are carried in.

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CHAPTER XV

MANUFACTURING SPECIAL TYPES OF NITROCELLULOSE

DYNAMITE COLLODION

COLLODION nitrocotton for manufact uring blasting gelatine and dynamite, also called dynamite cotton or dynamite collodion, is characterized by the very high viscosity of its solutions in organic solvents. It is produced by selecting a suitable cellulosic raw material, and performing the nitration at a low temperature, followed by a brief stabilization boil in a neutral or nearly neutral medium. The most important factor is the choice of suitable raw material.

Cellulosic raw materials. The best raw material for manufacturing dynamite nitrocotton is unbleached or very slightly bleached long-fibre cotton. Usually cotton wastes from spinning mills are used. The raw material is purified as described earlier (p. 363).

Too drastic purification should be avoided, as this can have an adverse effect on the product, lowering the viscosity of its solutions. Thus it is particularly undesirable to subject the cotton to bleaching.

Nitration. In order to keep the viscosity of the product as high as possible, the cotton is nitrated at a low temperature: 10–12°C. The reaction rate is not high at this temperature. It is therefore necessary to use a mixed acid relatively rich in nitric acid, for example:

HNO_3	22–24%
H_2SO_4	61–62%
H_2O	15–16%

The nitration is carried out in nitrators with mechanical stirring (or — in earlier days — in pots), the cotton to acid ratio being kept within the limits 1:45 to 1:50. In this way nitrocellulose containing 12.1–12.3% of N is obtained.

Stabilization. Dynamite nitrocotton, after being spun in the centrifuge, is immersed in the usual way in cold water, rinsed, and subjected to stabilization boiling. Stabilization must be carried out under conditions which make impossible to bring about a significant decrease of viscosity. Since a greater reduction of nitrocotton viscosity is caused by boiling it in acidified water than when it is boiled in pure water several preliminary boiling operations, carried out for short periods are

recommended. For instance, a series of three 2-hr boils, between each of which the water is changed, may be followed by one or more 4–8 hr boil also interspersed by a change of water. In some plants the product of nitration is first washed for 2 hr in hot water at 90°C (poaching), and is boiled several times for longer periods of time only after the acid has been removed.

Dynamite nitrocotton is pulped within as short a period of time as possible, e.g. 2 hr, because excessive beating of the product reduces the viscosity of the nitrocellulose solutions. The pulping is followed by washing or by a short poaching in boilers, after which the purity is checked by means of the heat test. After stabilization, the nitrocotton is freed from sand and other impurities.

Properties of dynamite nitrocotton. The most important test consists in dissolving dry dynamite nitrocotton in nitroglycerine in a porcelain dish at 65°C. To 97.5 g of nitroglycerine, 2.5 g of dynamite cotton are added. The ingredients are mixed for 20 min by means of a horn spatula. After being cooled the gelatine produced should be of such a consistency that it can be taken out of the porcelain vessel like a piece of dough. The gelatine should be neither too viscous, nor too fluid. Frequently an exudation test is carried out at a temperature slightly above room temperature. To this purpose a cylinder of gelatine is kept on a filter paper at 30–33°C for 144 hr. The relevent specifications in different countries allow different diameters for the liquid exuded into the fllter paper.

LACQUER-GRADE NITROCELLULOSE

Nitrocotton used for lacquer manufacture is characterized by the following properties:

(1) complete solubility in organic solvents, proved by its capacity to give clear solutions;
(2) a viscosity appropriate to the specific purpose for which it is intended.

The nitrogen content should be within the range 11.0–12.3% N, i.e. within such limits that ensure complete dissolution in organic solvents. For cheaper varnishes, in which ethyl alcohol is used as a solvent, nitrocellulose of lower nitrogen value, e.g. 10–10.5%, is used. Such a nitrogen content endows the product with complete solubility in ethyl alcohol.

Cellulosic raw materials. Linters or wood pulp cellulose are in use as raw material for manufacturing lacquer nitrocellulose. It is essential to use very well purified and bleached raw material. Wood cellulose should contain mainly α-cellulose. The admissible pentosan content is limited to traces only, because these compounds are a source of products insoluble in organic solvents. Cellophane can also be utilized for nitration.

An essential, important test is the measurement of the viscosity of a cuprammonium solution of the cellulose, as by this method it is possible to classify cellulosic material into grades suitable for manufacturing lacquer nitrocellulose of the desired viscosity.

Nitration. The nitration is usually carried out under conditions that promote the production of a low-viscosity product. Hence the process is carried out primarily with linters, at a relatively elevated temperature, commonly between 30 and 35°C. The clarity of nitrocellulose sulution increases with nitration time to an optimum and then decreases [1].

Stabilization. After being thoroughly washed free from acid, the nitrocellulose is subjected to stabilization either in boilers and afterwards in autoclaves (Fig. 153), or directly in autoclaves. Pressure boiling nitrocellulose in autoclaves makes it possible to control the viscosity of nitrocellulose with a high accuracy, since both time and temperature are controlled. The kiers for lacquer nitrocellulose manufacture are

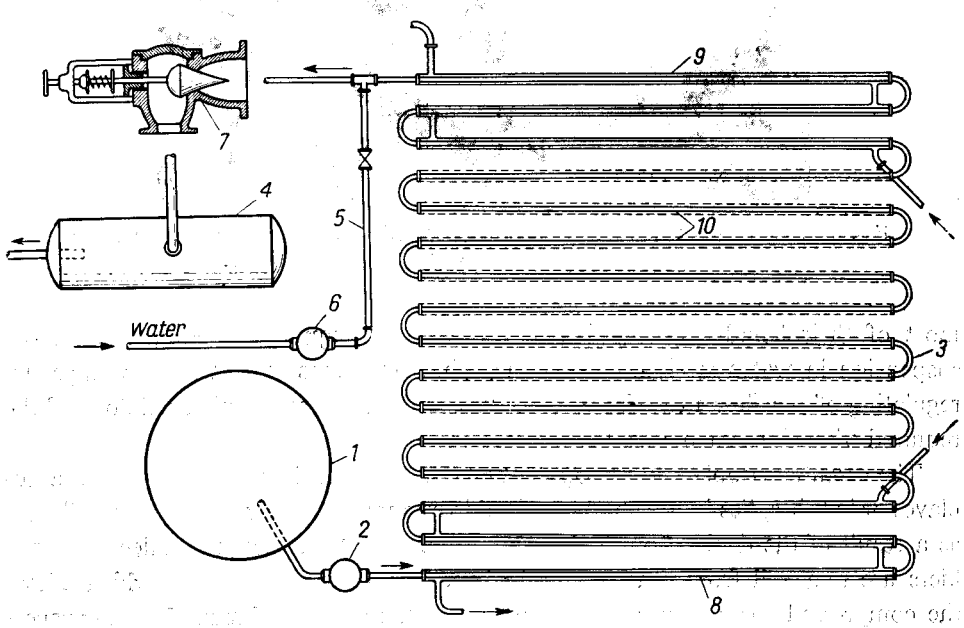

FIG. 164. Continuous digester for nitrocellulose, Hercules Powder Co., [2, 3]: *1*—mixer to prepare a slurry of nitrocellulose with water, *2*—pump, *3*—tube autoclave, *4*—collector of stabilized nitrocellulose, *5*—immergency water pipe with a pump (*6*), *7*—reduction valve, *8*—heated part, *9*—cooled part, *10*—insulated part.

constructed of stainless steel or welded sheet iron, enamelled inside. The capacity of the autoclaves ranges from 5 to 25 m^3, their charges varying from 400 to 1500 kg, at a nitrocellulose to water ratio of about 1:10. It is very important to ensure and maintain thorough mixing of the collodion cotton with the water, in order to prevent the nitrocellulose from getting dry, for this may cause decomposition, often followed by explosion. The autoclave is equipped with an external heating jacket as well as with a direct steam injection system.

A considerable advance in the practice of stabilizing lacquer nitrocellulose was made by the development of a continuous process of boiling under pressure in acid-resisting tubes, 100 mm dia., up to 1500 m long (Figs. 164 and 165). The tubes are warmed or cooled by means of outer jackets being heated throughout

FIG. 165. Continuous digester for nitrocellulose (Hercules Powder Co.) according to Milliken [2, 3].

most of their length, and cooled at the outlet. Lacquer nitrocellulose as a 4% suspension in water is circulated in the tubes by means of centrifugal pumps. By regulating of the flow rate, the temperature, and the pressure, nitrocellulose of the required viscosity can be produced.

The essential problem in the operation of kiering whether it takes place in autoclaves or in tubes, lies in the removal of acid vapours evolved from the nitrocellulose as a result of the denitration of unstable cellulose esters. Vapours collected in the kiers are removed from time to time by opening a gas-release valve which allows the compressed gases to pass into a special duct. In the continuous boiling process in pipes, the gases are entrained with the suspended nitrocellulose.

Great attention should be paid during the manufacture of lacquer nitrocellulose to the purity of the water used for washing and stabilization. The water should be carefully freed from iron, the maximum permissible concentration of which is 0.002 g/l. Water used in the production of film nitrocellulose should be of even higher purity and also must not contain calcium salts.

Bleaching. It is often necessary in the manufacture of lacquer nitrocellulose to remove all traces of coloured substances by bleaching. One method consists in oxidizing with potassium permanganate in the proportion of 1 kg $KMnO_4$ to 100 kg of lacquer nitrocellulose in the presence of a little sulphuric acid. After the reaction is over the nitrocellulose is rinsed with water, and the brown colour of manganese dioxide is removed by the action of sulphur dioxide or sodium sulphite.

It is also possible to bleach collodion by means of a 1% solution of chlorine or calcium hypochlorite applied for 30–60 min, after which the traces of chlorine are removed with sodium sulphite, and the product is washed.

CELLULOID-GRADE NITROCELLULOSE

Nitrocellulose of 11.8–12.3% N intended for celluloid manufacture is obtained in a way resembling the production of lacquer-grade material with the exception that the viscosity of the product is not of such decisive importance. Low viscosity of the nitrocellulose can cause the celluloid gel to be brittle, however. For this reason care should be taken to keep the viscosity above a certain limit. The essential stabilization can be carried out in boilers without recourse to autoclaves, but in order to shorten the stabilization process it is possible to carry out the kiering in autoclaves, the process then requiring only a few minutes.

LOW-GRADE NITROCELLULOSE

Recently interest was evinced in nitrocelluloses of very low nitration grade, e.g. 0.5–2.0% [4]. They were obtained by nitrating cellulose with mixtures containing 32% HNO_3, 31–38% H_2SO_4 and 32–37% H_2O at 8–30°C.

A noticeable degradation accompanies the reaction (lowering of molecular weight, appearance of carboxyl and carbonyl groups).

The most interesting property consists in their solubility in aqueous 6% NaOH at low temperature (e.g. —7°C). Products containing 0.9–1.0% N possess the best solubility. The viscous solutions can be used to form transparent film by treating with coagulating agents (e.g. C_2O) and washing with water (to remove alkali). The films possess high tensile strength and resistance to bending [5].

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CHAPTER XVI

NITRIC ESTERS OF POLYSACCHARIDES OTHER THAN CELLULOSE. NITRO-DERIVATIVES OF LIGNIN AND ABIETIC ACID

HEMICELLULOSES AND PENTOSAN NITRATES

EXPERIMENTS on the nitration of hemicelluloses composed mainly of pentosans were carried out by Will and Lenze [1]. These authors treated hemicelluloses with strong nitric acid, and isolated the nitration product by precipitation with water or sulphuric acid. The product obtained was insoluble in ether–alcohol.

Rassow and Dörr [2] nitrated hemicelluloses using the mixed acids applied for nitrating cellulose. Thus, making use of a mixture composed of

25.10%	HNO_3
66.85%	H_2SO_4
8.05%	H_2O

that normally produces nitrocellulose with a nitrogen content over 13%, they established that from hemicelluloses an insignificantly nitrated product was obtained in a small yield (Table 100).

The nitration products obtained by Rassow and Dörr were partially soluble in ether–alcohol, and completely soluble in amyl acetate.

As a result of nitrating hemicelluloses by means of more dilute acids, including 16.5–21.0% of water, at 20°C, a product containing even less nitrogen (5.8–7.2%) was obtained. It was scarcely soluble in mixtures of ether and alcohol.

Rassow and Dörr have also nitrated pure xylan, isolated from straw cellulose. By applying a concentrated nitrating acid, mixed at the proportions mentioned above they prepared nitroxylan in the form of a white powder containing 8.76% N, in 115.7% yield.

This product contains only 61% of substances soluble in ether–alcohol. This fraction contains 7.13% of nitrogen, whereas the nitrogen content of the insoluble part is 9.22% N. Other investigations in this field have been mentioned earlier, in Tables 89 and 90.

TABLE 100

THE RESULT OF NITRATING HEMICELLULOSE (AFTER RASSOW AND DÖRR [2])

Temperature °C	Nitrogen content of product %	Yield of nitro-hemicellulose produced from 100 g of hemicellulose g
20	7.24	50.75
10	8.30	107.5
0	8.88	113.2

PECTIN NITRATES ("NITROPECTINS")

Before World War II attempts were made in Germany to nitrate pectins prepared by extracting sugar beet shavings. However, the properties of the nitropectins were of no great interest, and they have not found any practical application.

Until recently, published data concerning pectic acid nitrates was lacking. Schneider and Ziervogel [3] obtained nitric esters of pectins as intermediate products which were then esterified by means of acetic anhydride to the corresponding acetates.

In 1949, Rogovin, Treyvas and Shorygina [4] prepared pectin nitric esters in order to investigate their properties. Pectic acid was nitrated for 4 hr at 20°C in a mixture composed of: 48% HNO_3, 50% H_3PO_4 and 2% P_2O_5 to yield a product containing 9.2% of nitrogen and 7.5% of carboxylic groups.

The number of COOH groups remained unchanged during nitration, and in contrast, say, with celluronic acid nitrates, the product is completely soluble in acetone. In order to explain this behaviour Rogovin *et al.* suggest that a part of the carboxyl groups in pectic acid are esterified, and therefore incapable of participating in ester cross-links between carboxyl and hydroxyl groups. These links are mentioned by the same investigators while discussing the structure of celluronic acids (see below).

ALGINIC ACID NITRATES

Rogovin, Treyvas and Shorygina [4] have examined the product of nitration of alginic acid obtained after 4 hr at 20°C by means of a mixed acid consisting of: 48% HNO_3, 50% H_3PO_4, and 2% P_2O_5.

The product contained 9.3% N and 16% COOH. During nitration the number of carboxylic groups did not increase. The product was almost completely soluble in acetone (96.4%).

To explain the appreciable solubility of the product, Rogovin *et al.* suggest that the carboxylic groups of alginic acid are probably internally esterified with hydroxyl groups. Thus (as with pectic acid nitrates, see above) no cross-links can be formed of the type assumed by the same authors to exist in celluronic acids and in celluronic acid nitrates (see below).

CELLURONIC ACID (CARBOXYCELLULOSES) NITRATES

Celluronic acid produced by treating cellulose with nitrogen tetroxide may then be esterified by means of nitric acid. It has been found that even in the presence of small number of carboxylic groups a considerable change in the properties of the nitric esters is brought about, as compared with cellulose.

To characterize the properties of the product of esterification by means of nitric acid, Rogovin, Treyvas and Shorygina [4] have determined the values collected in Table 101.

TABLE 101

THE RESULT OF NITRATING CELLURONIC ACID (AFTER ROGOVIN, TREYVAS, SHORYGINA [4])

Content of COOH groups in the original substance %	Nitrogen content of product %	Solubility in acetone %
1.56	13.5	18.2
3.6	13.0	9.7
8.0	11.5	13.2
18.5	7.0	2.5

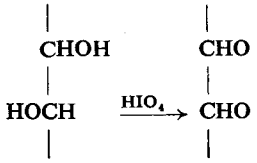
It is clear from the figures that owing to the presence of 2–3% COOH, i.e. one carboxylic group for 8–10 anhydroglucose rings, the product is made very poorly soluble even in such a good solvent of nitrocellulose as acetone.

As for the negligible solubility of celluronic acid nitrates, Rogovin *et al.* consider that it is brought about by the formation of cross-links between the neighbouring long-chain-molecules of oxidized cellulose, owing to the participation of carboxylic groups and free hydroxylic groups. The strength of the glycosidic bonds that link the anhydroglucose units together is considerably weakened by a partial substitution of the primary alcoholic groups by carboxylic groups. Thus, carboxycellulose containing 2–3% of COOH undergoes de-polymerization in the presence of dilute alkalis even at room temperature.

DIALDEHYDE CELLULOSE NITRATES

In the anhydroglucose units of cellulose oxydized by means of periodic acid two aldehyde groups are present produced as a result of the oxidation reaction

of the neighbouring secondary alcoholic groups (α-glycols) detected by Hudson and Jackson [5]:



Rogovin, Yashunskaya and Shorygina [6] have studied the products of esterification of dialdehyde cellulose by means of nitric acid. The raw material, containing various quantities of aldehyde groups, was nitrated at 0°C with mixture composed of 48% HNO_3, 50% of H_3PO_4 and 2% of P_2O_5.

The product is distinguished from nitrocellulose by its higher hygroscopicity and poorer solubility in organic solvents. Data illustrating the point are listed in Tables 102 and 103.

TABLE 102

THE HYGROSCOPICITY OF ALDEHYDE CELLULOSE NITRATES

Degree of oxidation (number of aldehyde groups contained in every 100 anhydroglucose units)	Nitrogen content of product %	Hygroscopicity (absorbed water) %
0 (cellulose)	13.85	0.82
7.0	13.66	1.02
43.8	12.69	2.64
72.0	11.91	3.50
144.6	9.42	11.02

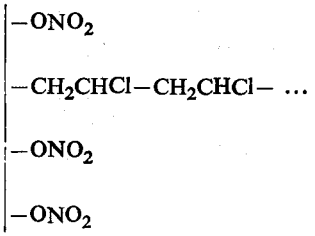
TABLE 103

THE SOLUBILITY OF ALDEHYDE CELLULOSE NITRATES

Degree of oxidation	Nitrogen content of the product %	Solubility in acetone %
0 (cellulose)	13.85	100
5.2	13.75	44.4
14.0	13.11	27.6
43.8	12.7	3.4
73.3	11.8	3.8
117.4	10.3	3.3
144.6	9.4	1.6

COPOLYMERS OF NITROCELLULOSE

Recently Kargin, Usmanov and Aikhodzhayev [7] prepared a grafted copolymer of nitrocellulose with vinyl chloride or vinylidene chloride. The method roughly consists in the formation of free macro-radicals of nitrocellulose (through γ-irradiation or — more effectively — ozonization of nitrocellulose). After that, the monomer of vinyl chloride or vinylidene chloride is reacted with the macro-radical in the presence of a redox catalyst. This eventually gives a copolymer of the following diagrammatic structure:



The main property of such a copolymer is a much lower ignitability and combustibility than that of nitrocellulose. This may be of value in making heat resistant and non-inflammable films, lacquers, celluloid, etc.

On cross-linking nitrocellulose — see p. 303.

NITROSTARCH

Braconnot, who first nitrated cellulose, was also the first to nitrate starch, in 1833 [8]. He dissolved potato meal in conc. nitric acid, and then precipitated the nitration product by adding water. These experiments were repeated by Pelouze [9] and Buijs Ballot [10], whereas in an experiment of Rheinsch [11] the starch was nitrated like cellulose in modern methods, by means of a mixture of nitric and sulphuric acids. For a long time nitrostarch was not distinguished from nitrocellulose. Eventually, attention was drawn to their difference by Béchamp [12]. By reduction of starch nitrate he recovered the initial carbohydrate, i.e. starch in a form that differed from the non-nitrated original starch by its solubility in water. (In accordance with our knowledge it was most probably dextrin). Béchamp [13] tried to apply various methods for isolating nitrostarch dissolved in nitric acid. He used both water and sulphuric acid, and obtained nitrostarch with different nitrogen contents, and has observed that the product separated by means of sulphuric acid was the less stable, readily undergoing spontaneous decomposition. Mühlhäuser [14] expressed a far-sighted view that the low stability of this nitrostarch was due to partial sulphonation brought about by sulphuric acid.

The most extensive of the researches carried out in the nineteenth century were those of Mühlhäuser [14], who dissolved starch in a ten-fold quantity of nitric acid, sp. gr. 1.50 and precipitated the product with thirty times as much sulphuric acid. In this way he introduced 13.5% N, but the nitration product was unstable.

Experimenting with a still stronger nitric acid, sp. gr. 1.52, Will and Lenze [1] prepared nitrostarch characterized by a nitrogen content of 14.04%. They established that it is possible to produce nitrostarch of high nitrogen percentage and adequate stability providing it is subjected to a stabilization boil in ethyl alcohol.

Moreover, Will and Lenze established that starch can be nitrated in a manner resembling cellulose nitration, by means of a mixture of nitric and sulphuric acid, to obtain a product containing 13.9% N. The same method was tried by Sapozhnikov [15]. However, he did not wholly confirm the results published by Will and Lenze, since the maximum nitrogen content in his product was 13.5%.

Starch nitrated by Brown and Millar [16], by dissolution in nitric acid and subsequent precipitation with the help of sulphuric acid, was stabilized by washing in ether and chloroform.

Soluble starch was nitrated by Syniewski [17]. The most extensive published researches devoted to the preparation, purification and properties of nitrostarch are those of Hackel and T. Urbański [18].

Theoretical experiments with nitrostarch attracted the attention of technologists. Uchatius [19] worked out a commercial method of nitrostarch manufacture in 1861 and proposed the use of nitrostarch as a propellant.

Patents were granted in 1889–90 to Schücker [20] for smokeless powder consisting of nitrostarch and oxidizing substances as saltpetre or potassium chlorate, while a patent for manufacturing nitrostarch was granted to Dynamit A.G., Alfred Nobel, in 1891 [21]. This proposed the nitration of starch by dissolution in a tenfold amount of nitric acid, followed by precipitation of the product by means of spent acid from nitroglycerine manufacture. Subsequent operations comprised washing with water, aqueous sodium carbonate, and aqueous aniline. According to Snelling [22] the production of nitrostarch started in the U.S.A. in about 1888, under the name "Volney's powder".

Initially nitrostarch could not be used in practice due to its inadequate chemical stability, but by the beginning of the present century nitrostarch had found practical application in the U.S.A., where it was introduced by a British chemist, Hugh [24] who in 1900 and 1903 constructed and set in operation two nitrostarch factories: one near Asburg Park, New Jersey, and the other near Wharton. Hugh advertized "non-freezing Hugh's Powder" as a substitute for dynamite. It has been proved to be pure nitrostarch.

To nitrate starch, Hugh treated it with an anhydrous mixture of nitric acid, sulphuric acid and oleum to obtain a product that very probably contained 13.3–13.5% N. Hugh's plant was destroyed as the result of an explosion, and the manufacture and application of Hugh's powder was abandoned. Further development of nitrostarch was then taken up by du Pont [25]. In 1905 this company introduced a low-freezing explosive "Nyalite". A similar low-freezing explosive material "Arctic", introduced by the same firm in 1907, was manufactured for the next decade. Both contained nitrostarch.

Another corporation engaged in the same manufacture of nitrostarch for com-

mercial mining purposes was the Trojan Powder Co. [25], which remained for many years the largest and most important producer of nitrostarch.

Another major manufacturer was the Eastern Dynamite Corporation, at Wilmington, Delaware, which developed the patents of Holmes [26]. The starch was nitrated by means of mixed nitric–sulphuric acid and then stabilized by prolonged boiling with water in the presence of calcium carbonate, for 75–100 hr. In later patents the addition of ammonium salts to the water was recommended.

Sadtler [27] lays particular stress on the purification of the starch prior to nitration.

In the period after World War I the efforts of the Trojan Powder Co. to improve the chemical stability of nitrostarch were continued, and a series of patents was granted (Waller [28]).

Special care was devoted to the manufacture, stabilization and application of nitrostarch in the Trojan Powder Co. under the direction of Snelling. His work during the period from 1918 to 1945 is embodied in a large number of patents [29].

Further, a noteworthy patent describing the nitration of starch in the form of flakes was obtained by Norman of the Hercules Powder Co., in 1933 [30].

Towards the end of World War I some 25,000 tons of nitrostarch per annum were manufactured in the U.S.A. It was used mainly in the form of two explosive materials: Grenite and Trojan Explosive. The composition of these explosives is given in Vol. III.

In the period between the two World Wars the production of nitrostarch on an industrial scale also started in Hungary and Poland.

At the beginning of World War II nitrostarch explosives were used for filling bombs, but this practice ceased when the output of trinitrotoluene reached adequate volume. Serious interest was roused, on the other hand, in Trojan's Nitrostarch Demolition Explosive. Its composition is reported in Vol. III.

In Hungary nitrostarch explosives were used during World War II for filling hand grenades.

An extensive review of the literature on nitrostarch was given by Caesar [23].

GENERAL CHARACTERISTICS OF STARCH

Starch is a plant product composed of polysaccharides having the general formula $(C_6H_{10}O_5)_n$. Usually starch is diffused in the form of granules, differing in shape and dimensions according to the particular plants in which the starch occurs. Despite such morphological and physical differences (i.e. in the molecular size) the chemical properties of starches of different origin are the same in principle.

A basic characteristic, common for all kinds of starch, is its aptitude to undergo hydrolysis. Because of this property it is one of the fundamental elements of the diet.

In all types of starch small amounts of phosphorus are present owing to the part played by phosphoric compounds in the enzymatic processes of starch formation. Disregarding a few exceptions, starch consists of two fundamental components:

amylose and *amylopectin*. The separation of these components can be achieved roughly by means of hot water (70°C) which dissolves amylose (10–20%) but is incapable of dissolving amylopectin (80–90%). As a result of hydrolysis these substances yield *maltose*, resulting from an enzymatic breakdown, or *glucose*. The components of starch can be distinguished by means of the iodine test; amylose in the presence of iodine is coloured blue, whereas with amylopectin the colour is violet to red-violet. In comparison with amylose, amylopectin is more resistant to the action of enzymes. Thus in the presence of β-amylase, the amylose is completely hydrolysed to maltose, whilst amylopectin undergoes hydrolysis only to the extent of some 60%.

From osmotic pressure measurements, the molecular weight of amylose has been determined as approximately 10,000–50,000. This value is well in line with the value estimated from the determination of the terminal functional groups.

The molecular weight of amylopectin is appreciably higher, since according to osmotic pressure determinations it is 50,000–1,000,000.

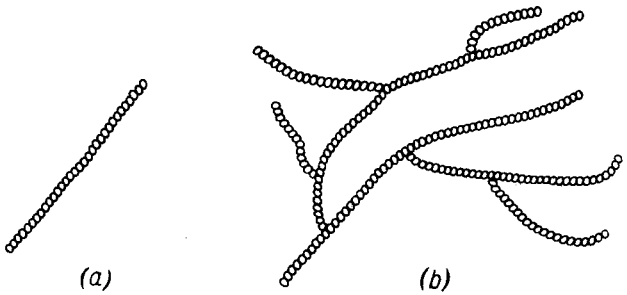
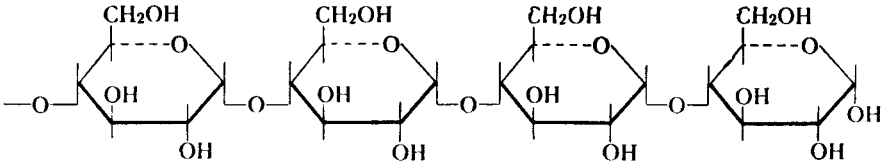


FIG. 166. Structure of amylose and amylopectin: *a*—amylose, *b*—amylopectin.

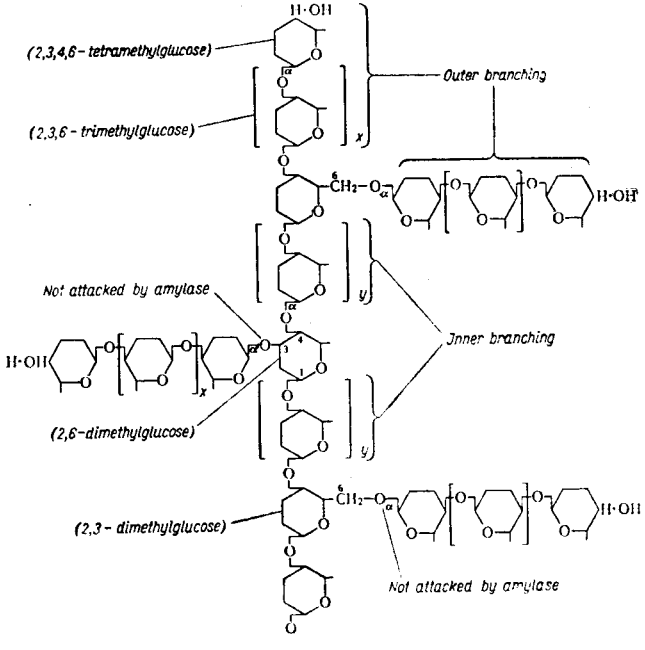
From the determination of the end groups, the long-chain molecules of amylopectin seem to be composed of 24–30 glucose units, from which it is concluded that the substance is a branched-chain carbohydrate.

On the basis of researches devoted to the products of partial or total hydrolytic breakdown of methylated starch, the chain of α-D-anhydroglucose is thought to constitute the main element of the amylose and amylopectin molecules. These units are combined as in maltose, i.e. by means of α-glucosidic linkages formed between the carbon atoms 1 and 4:



As a result of hydrolysing methylated starch, in addition to the main product, which is 2,3,6-trimethylglucose, a small amount of 2,3,4,6-tetramethylglucose is formed from the end rings.

Similarly, the hydrolysis of methylated amylopectin yields small quantities of 2,3-dimethylglucose and its isomeric ether, probably 2,6-dimethylglucose. The presence of the last two compounds confirms the branching of the chains (Fig. 166) at carbon atom 6, and perhaps 3. Staudinger [31] has therefore proposed the following formula for amylopectin (reproduced according to L. F. Fieser and M. Fieser [73]):



PHYSICAL PROPERTIES OF NITROSTARCH

According to Hackel and T. Urbański [18] the solubility of nitrostarch is dependent on its nitrogen content.

Nitrostarch containing 8.0–12.8% N dissolves completely in ether–alcohol, but products with a nitrogen content of over 12.8% N are only partially soluble. In the instance of 13.1% N the solubility amounts to about 78%.

Nitrostarch characterized by a nitrogen content below 8.0% is scarcely soluble in ether–alcohol. Thus the solubility of a 6.4% N-product is only 8.4%.

Nitrostarch dissolves in alcohol more easily than nitrocellulose, and at a nitrogen content of 10.0–11.5% is wholly soluble in ethyl alcohol. Incomplete dissolution indicates nitrostarch of higher or lower nitrogen percentage. A product containing 12.1% N has a solubility of 32.5%.

As shown by the experiments of Hackel and T. Urbański, all nitrostarch containing 6.4% of N or more dissolves entirely in acetone.

Kołaczkowska and T. Urbański [32] on the basis of X-ray investigations attempted to explain the crystallographic transformations suffered by starch as result of nitration. They used nitrated potato starch and soluble starch in this investigation.

In the X-ray diagram of potato starch, a series of rings was discovered. Using the nomenclature of Katz [33] these are typical of the "B-spectrum" (Fig. 167a). The spectrum of soluble starch resembles the spectra of amorphous substances (Fig. 167b).

It has been proved that nitrostarch produced by the nitration of potato starch,

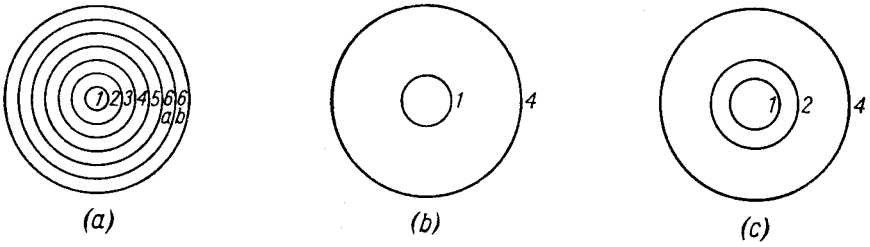


FIG. 167. X-Ray diagrams of natural potato starch (a), soluble starch (b), nitrostarch (c).

and the product of nitrating soluble starch, gave exactly the same picture shown in Fig. 167c for which Kołaczkowska and Urbański suggested the name of "N-spectrum".

From these experiments the authors concluded that the nitration of raw starch entailed a decrease in its structure regularity. Amorphous starch, on the contrary, acquired a more regular stucture as the result of nitration.

These experiments also suggest that nitration of starch passes through the stage of hydrolysis to soluble starch before being nitrated:

$$\text{Starch} \xrightarrow{HNO_3} \text{soluble starch} \longrightarrow \text{nitrostarch}$$

This is supported by the examination of the viscosity of nitrostarch which indicates strong degradation of the starch molecule in the course of nitration.

The viscosity of nitrostarch solutions is appreciably lower than the viscosity of the corresponding nitrocellulose solutions. Taking the viscosity of water as 100, the viscosity of 1% nitrostarch solutions varies within the relative values of 45 and 70. Due to such low viscosity and non-oriented crystal structure, nitrostarch solutions leave very fragile film after evaporation. Hence nitrostarch is valueless for varnish production, and for smokeless powder making.

In principle the viscosity of nitrostarch is affected by the same factors which cause a change of viscosity in nitrocellulose. Thus a high nitrogen content in the product, an elevated nitration temperature, or an intensive stabilization boiling of the nitrated product lowers the viscosity of the nitrated substance. However, in the case of nitrostarch the changes in viscosity under the influence of these factors are insignificant.

The data collected below illustrate the behaviour of nitrostarch obtained by treatment with nitric acid alone, without any admixture of sulphuric acid (Table 104).

There is no doubt that starch is strongly degraded during nitration owing

TABLE 104

THE RELATIONSHIP BETWEEN THE NITRATING CONDITIONS AND THE PROPERTIES OF NITROSTARCH

Temperature of nitration °C	Nitrogen content of nitrostarch %	Relative viscosity (water = 100)	Solubility in alcohol %
20	12.13	58.4	32.5
	11.09	52.7	100
	10.28	50.7	78.2
	9.51	50.3	41.8
0	13.19	71.6	
10	13.08	68.3	
20	12.76	61.7	
30	12.57	57.3	

to the hydrolytic action of nitric acid. This is demonstrated by the rapid decrease in viscosity of a 10% starch solution in 97.3% nitric acid, at a temperature of 20°C, as reported by Hackel and T. Urbański [18]:

after the lapse of:	relative viscosity (water = 100)
45 min	4730
75 min	3530
2 hr	2720
3 hr	1925
6 $\frac{1}{4}$ hr	1040
12 hr	625
24 hr	415

On account of such strong degradation, the viscosity of nitrostarch solutions is low whatever the preparative method applied. Likewise large differences in the viscosities of starch before nitration exert practically no influence on the viscosity of the nitrated product. Experiments carried out by T. Urbański and Gołofit [34] provided the data needed to determine the viscosity of starch (in Parlow degrees) and the viscosity of nitrostarch obtained by nitration with nitric acid, sp. gr. 1.50, followed by precipitation with water. The results are collected in Table 105.

The degradation of nitrostarch is also considerable, if starch is nitrated by means of a mixed acid composed of nitric and sulphuric acid. On the contrary, application of nitrating mixture consisting of nitric acid and ortho-phosphoric acid makes it possible to obtain a product nearly twice as viscous as that obtained by treatment with a mixture of nitric and sulphuric acid (T. Urbański and Kapuściński [36]). This shows that the mixture of nitric and phosphoric acid causes less degradation of starch than nitric acid alone or mixed with sulphuric acid. Previously, Berl and Kunze [37] had come to the same conclusion. They found the product of

TABLE 105

COMPARISON OF THE VISCOSITIES OF STARCH AND NITROSTARCH (AFTER T. URBAŃSKI AND GOŁOFIT [34])

Type	Starch		Nitrostarch	
	Viscosity in Parlow degrees	Relative viscosity (water = 100)	Nitrogen content %	Relative viscosity (water = 100)
1	224	1415	13.3	138
2	165	707	13.2	136
3	151	560	13.1	134
4	144	471	13.3	131
5	122	319	13.2	132
6	99	232	13.2	131
soluble	14	103	13.3	124

nitration with a mixture of nitric and phosphoric acid to be of significantly higher viscosity. Later it was confirmed by Kunz *et al.* [37a). They determined the mean molecular weight of starch nitrated with nitric acid–phosphoric acid–water (64/26/10) and nitric acid–sulphuric acid–water (70/20/10) mixtures and found the relative figures 100 and 21–43, respectively.

The nitration product of starch is a non-homogeneous substance. Nitrostarch may be divided into fractions by adding water to its solution in acetone as demonstrated by T. Urbański and Cieślak [38]. The individual fractions vary slightly in respect of nitrogen content, whereas their viscosity is almost identical.

Ashford, Cook and Hibbert [39] have found that it is possible to divide nitrostarch into a soluble fraction of low nitrogen content, and an insoluble fraction containing up to 13.9% N by boiling nitrostarch in alcohol.

A further factor that causes the non-homogeneity of nitrostarch is the presence of the two components, amylose and amylopectin in starch. It has been demonstrated by nitrating each of these starch components separately that the nitration products differ from one another. Berl and Kunze [37] detected that amylopectin yields a product of a considerably higher viscosity than that resulting from the nitration of amylose. This effect may be attributable to the higher molecular weight of amylopectin.

However, T. Urbański and Berłowski [40] have not confirmed this observation and in fact they report that either of these substances give products of more or less the same viscosity. This could occur in consequence of extensive hydrolysis during nitration.

The solubility of the amylose nitration product in ether–alcohol was reported (Ashford, Cook and Hibbert [39]) to be lower, e.g. 20%, than that of the nitration product of amylopectin, which is 86–87%. Such behaviour is explicable in terms

of the branched structure of the latter, on the general principle that the solubility of all branched-chain polymers, *except space-network polymers*, is higher than that of straight-chain ones. According to Ashford *et al.* nitroamylose is more stable than amylopectin.

THERMOCHEMICAL AND EXPLOSIVE PROPERTIES OF NITROSTARCH

D. Smoleński and Strzondała [41] determined the heat of combustion of nitrostarch of various nitrogen percentage and hence estimated the heat of formation of nitrostarch, for nitrostarch obtained both by nitration in mixed acid (Table 106) or in nitric acid alone (Table 107).

TABLE 106

NITROSTARCH PRODUCED BY MEANS OF MIXED ACID

Nitrogen content %	Heat of combustion cal/g	Heat of formation cal/g
10.52	2575.8	702.4
11.02	2510.6	668.3
12.87	2276.7	555.5
13.24	2217.9	541.0

TABLE 107

NITROSTARCH PRODUCED BY MEANS OF NITRIC ACID ALONE

Nitrogen content %	Heat of combustion cal/g	Heat of formation cal/g
10.52	2580.7	696.5
12.20	2378.4	576.3
12.87	2309.0	523.3
13.34	2273.3	504.5

The differences in values between the two kinds of nitrostarch are regarded by the authors as related to the presence of sulphuric esters in the nitrostarches prepared by means of mixed acids.

Nitrostarch when ignited burns readily in a way similar to nitrocellulose.

Data characterizing the explosive properties of nitrostarch have been published by Hackel and T. Urbański [42] for nitrogen contents from 7.7% to 13.4% N.

Le Roux [42a] examined explosive properties of nitrostarch of 13.52% N. At a density of 0.90, a charge of 30 mm dia. in a cardboard tube detonated at the rate of 4970 m/sec. The relative lead block expansion was 117 (picric acid = 100), i.e. much the same as for nitrocellulose of 13.40% N.

TABLE 108

EXPLOSIVE PROPERTIES OF NITROSTARCH (AFTER HACKEL AND T. URBAŃSKI [42])

No.	Nitrogen content %	Rate of detonation (in a pipe of diameter 34/28 mm), $d = 0.88$, initiation by		Lead block test cm^3	Sensitiveness to shock; 8% explosions caused by a 5-kg weight falling from a height of cm
		No. 8 detonator	10 g of picric acid		
1	13.4	6190	—	430	21
2	13.1	5740	—	395	23
3	12.8	5300	—	375	—
4	12.4	4950	—	360	36
5	12.1	4480	—	320	38
6	11.6	3880	—	300	70
7	11.0	3020	—	260	100
8	10.5	2880	—	230	100
9	9.4	1500	3200	160	100
10	8.9	1000	3000	125	100
11	7.7	does not detonate		35	does not explode

NITRATION OF STARCH

A fundamental difference between starch and cellulose is shown by their behaviour in the presence of nitric acid. Starch brought into contact with nitric acid of over 76% concentration swells and eventually dissolves, whereas cellulose swells only insignificantly and generally does not dissolve (as described already it can only be dissolved in nitric acid of *ca.* 80% HNO_3).

When a nitrostarch solution in nitric acid is poured into water, sulphuric acid or phosphoric acid, the nitrostarch is precipitated as an amorphous powder.

Hackel and T. Urbański [18] reported that a solution of starch in 10 times its weight of nitric acid (97.3% HNO_3) poured after 6 hr at 20°C into 20 times its weight of water yielded a nitrostarch of 11.7–11.9% N almost completely soluble in alcohol and ether–alcohol. The method has not come into practical use as the dilution of nitric acid with water is not economic.

Nitrostarch of 12.6% N can be prepared, if starch dissolved in ten-fold quantity of nitric acid is poured into 40 times its volume of 94% sulphuric acid, at a temperature not exceeding 20°C. Such nitrostarch includes 11.4% of substance soluble in alcohol, and 95.7% of substance soluble in ether–alcohol.

Starch exposed to the action of nitric acid for a period shorter than 6 hr is converted into nitrostarch of lower nitrogen content, e.g. 12.2% N, after 4 hr.

The main reason why this procedure has not been developed commercially is that during the precipitation of nitrostarch by means of sulphuric acid a sticky intermediate product separates. This is difficult to mix, hence it is not easy to keep its temperature constant and correct, and its composition uniform. In consequence

of local overheating, local denitration often takes place so that the product always has a lower nitrogen content than one nitrated directly in a mixture of nitric and sulphuric acid.

Nitration in a mixture of nitric and sulphuric acid results in a more homogeneous product. The maximum nitrogen content is attained after 1–2 hr. As in the case of nitrocellulose, the nitrogen content depends on the final composition of the nitrating acid, i.e. on two factors:

(1) the composition of the mixed acid,

(2) the ratio of mixed acid to starch.

In order to determine the relationship between the nitrogen content of nitrostarch and the composition of the nitrating mixture, Hackel and T. Urbański [18] examined the nitration of starch by means of over a hundred mixed acids of different composition. The starch was nitrated for 1 hr in 50 times as much nitrating acid at 10–12°C. The results obtained can be depicted in a triangular diagram HNO_3–H_2SO_4–H_2O. The composition of the acid is given both in mole per cent, and in weight per cent (Figs. 168a, b).

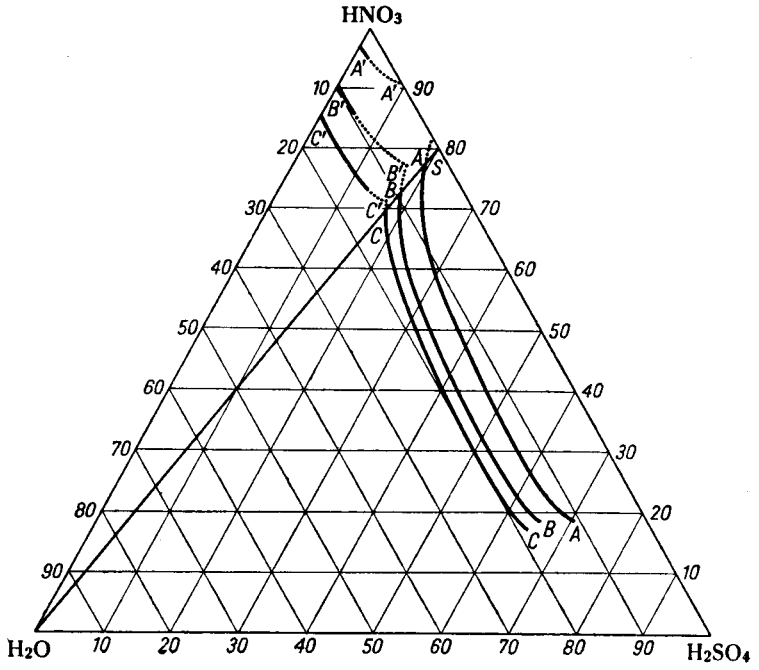
The region of mixtures between the curve *AAA'A'* and axis HNO_3–H_2SO_4 corresponds with nitration to a nitrogen content of more than 12.75% N. In the area limited by *AA–BB* and *A'A'–B'B'* respectively, there are values that correlate with mixed acids yielding products of 11.1–12.75% N. Between *BB–CC* and *B'B'–C'C'* respectively, products of 9.15–11.1% N are obtained. To the left of the line *CC* lies an area corresponding to nitrating acids that give non-homogeneous, low-grade nitrated, oxidized or hydrolysed products. The outlines of the curves *AA*, *BB*, *CC*, resemble those for nitrocellulose (Fig. 121) and also those for nitronium ion $NO_2^{\oplus}$ concentrations.

Comparison of the Sapozhnikov graph for nitrocellulose with the graph by Hackel and T. Urbański shows that in the latter the curve has a minimum which corresponds approximately with a mixed acid where the nitric acid to sulphuric acid weight ratio is about 6 (mole ratio is about 9).

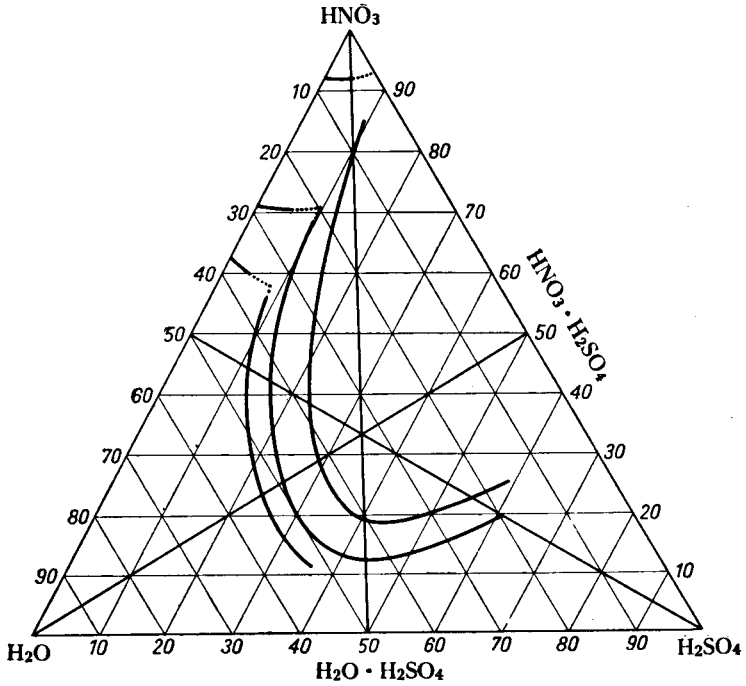
All mixed acids made up with a HNO_3:H_2SO_4 weight ratio exceeding 6, i.e. poorer in sulphuric acid, favour the production of nitrostarch of higher nitrogen percentage. This can be demonstrated by the slope of the lines *A'A'*, *B'B'*, *C'C'*, and is explained by the fact that mixtures confined to those areas dissolve the starch during nitration, which therefore proceeds not as a two-phase system as with most mixtures, but in a single phase, so that the nitrating action of these mixtures is more intense. Only towards the end of the nitration process a certain amount of nitrostarch is precipitated from certain mixed acids.

Further, the hydrolysis of starch nitrate in acids containing little or no sulphuric acid does not proceed to such a large extent as is usual when starch is treated with mixtures of high sulphuric acid content.

In all experiments with nitrating acid prepared by mixing nitric and sulphuric acid at a weight ratio higher than 6, the nitrostarch was separated by drowning the whole in water.



(a)



(b)

FIG. 168. Triangular diagram of nitration of starch, according to Hackel and T. Urbański [18]: (a) in mole %, (b) in weight %.

By nitrating different types of starch by means of mixed acid Staudinger and Eilers [43] obtained a product containing 12.5% of nitrogen. Staudinger and Husemann [44] followed the degradation of starch during its nitration.

An interesting nitration method according to which starch was nitrated in two stages at 5°C for 30 min by means of a nitrating mixture including 75–90% of nitric

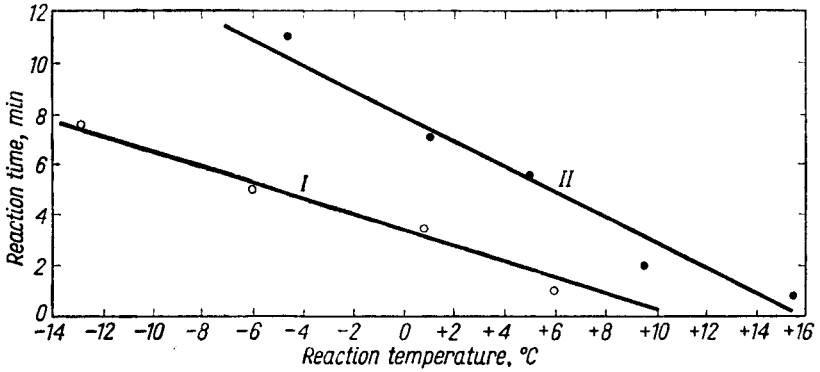


FIG. 169. Reaction time of nitration of starch as a function of temperature, according to Kunz and Tóth [46].

acid, was worked out in the Hungarian factory "Nitrokemia" [45]. Nitration was carried out in two stages. The patents claim that this improves the chemical stability of the product.

Recently extensive investigations on the nitration of starch, mainly by using mixed nitric and sulphuric acid have been carried out by Kunz and Tóth [46]. Their object was to determine the effect of the ratio of the components in the nitrating mixture and the activity of nitric acid in the mixtures on the nitrogen content of the nitrostarch, the heat of esterification, and the relation between the nitration temperature and the viscosity of the product. Their observations concerning the time of reaction are of special interest. This varies as a linear function of the nitration temperature. In the graph (Fig. 169) the relationship is shown for two mixed acids:

(I) 35.0% HNO_3, 57.5% H_2SO_4, 7.5% H_2O,
(II) 33.4% HNO_3, 60.75% H_2SO_4, 5.81% H_2O.

At temperatures of +14°C and over a product nitrated to the maximum nitrogen content is obtained almost immediately.

T. Urbański and Kapuściński [36] investigated the nitration of starch in a mixture consisting of nitric acid and phosphoric acid, and found that mixed acids containing *ca.* 10% of water or more caused the starch to swell so that nitration proceeded unevenly. Using an anhydrous mixed acid, for instance composed of 20% of HNO_3 and 80% of H_3PO_4, nitrostarch containing 13.0–13.1% of nitrogen was obtained. This is compatible with the results of earlier experiments by Berl and Kunze (37].

It has been demonstrated (T. Urbański and Janiszewski [47]) that it is possible to nitrate starch by means of nitric anhydride vapour in a stream of air or with

nitrogen pentoxide dissolved in nitric acid. By nitration for 1 hr starting with 30 min at 10°C, and finishing at 16°C, a product containing as much as 13.86% of nitrogen, characterized by a high chemical stability, was prepared.

During World War II the nitration of starch by means of nitrogen pentoxide was investigated by Caesar *et al.* [48]. They used N_2O_5 dissolved in chloroform. In the course of the reaction nitric acid was formed, which partially dissolved the nitrostarch. In order to counteract this disadvantage the authors added sodium fluoride, which bound the nitric acid by a hydrogen bond to form a complex compound Na—F···· HO—NO_2. In this way they succeeded in achieving practically complete substitution of the hydroxyl groups and thus obtained starch trinitrate of low degradation. Its nitrogen content was 13.92–14.03%. No sulphuric esters being present, the stabilization of this product did not present any difficulties.

Later these results were confirmed by Vollmert [49].

According to Izraelashvili [50] nitration conditions favourable for yielding an ester of high nitrogen percentage occur if the concentration of nitronium ions $NO_2^{\oplus}$ in the nitrating agent is high.

Hackel and T. Urbański [18] examined starch derived from different plants (maize, wheat, rice, tapioca and potato) and on reaction with mixtures of nitric and sulphuric acid they obtained nitric esters of practically identical properties (i.e. of the same nitrogen content, solubility, and viscosity) providing the degree of purity of the starch was the same.

COMMERCIAL METHODS OF NITROSTARCH MANUFACTURE

The methods of manufacturing nitrostarch on an industrial scale are not reported in any detail in the technical literature, since for most of them are kept secret.

A solitary description of a commercial method in use in the U.S.A. was published by Davis [51]. To prepare starch for nitration it is first freed from oils and pectic acids by washing in a dilute solution of sodium or ammonium hydroxide, and then rinsing with water. The starch is then dried to a moisture content of below 0.5%, and nitrated.

As the nitrating agent, mixed acid composed of

38%	HNO_3
62%	H_2SO_4

is used.

A charge of about 90 kg of starch is nitrated in one operation. It is immersed in some 360 kg of acid warmed to 32°C. The nitrator is equipped with stirrer. During the operation the temperature is kept within the limits 38–40°C. At the end of nitration the contents of the nitrator are drowned into a tank with water, and the separated product is filtered from the acid.

The nitration product is purified by washing in cold water, without boiling. In order to neutralize acid, in the first stage of washing ammonia is added. Timely application of ammonia is very important for stabilization, since ammonia is readily

absorbed by the grains of nitrostarch. The product is dried at a temperature of 35–40°C. Its nitrogen content is 12.75%.

There are many questionable points in this description. To begin with, the dilution of the batch by plunging into water is uneconomic. This can also easily cause denitration of the product owing to local overheating. A stabilization method that omits boiling does not, in general, yield a product of satisfactory stability.

STABILIZATION OF NITROSTARCH

The problem of how to stabilize nitrostarch has been solved by different means, but the majority of stabilization processes remain obscure as patent secrets. None the less, from certain observation some general conclusions can be made. It was early observed by Béchamp [13] that nitrostarch obtained by nitration in nitric acid alone is more stable than one obtained by means of nitric acid mixed with sulphuric acid. This has been confirmed experimentally by Hackel and T. Urbański [18], and seems likely to be explained by the formation of starch sulphates or mixed nitric and sulphuric esters of starch.

One of the nitrostarch stabilization methods worked out by Hackel and T. Urbański (unpublished) consisted in giving the nitrostarch a very finely divided form so as to make it possible for water to invade the interior of the nitrostarch granules. It is, in fact, a method very similar in principle to the process of stabilizing nitrocellulose, since the fundamental operation in the latter consists in cutting the nitrocotton fibres into shorter pieces so as to open the interior of the fibres and permit water to penetrate.

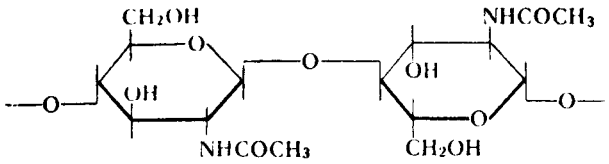
The other principal operation in the stabilization of nitrostarch is prolonged boiling, initially in acid water, and finally in alkaline water. As in the stabilization of nitrocellulose premature alkalization of the stabilizing medium is not recommended as this hinders the hydrolysis of sulphuric esters. Nevertheless in some American contributions (as mentioned above) early addition of ammonia for washing nitrostarch is reported to favour the formation of a stable product.

In patents granted to the Hungarian plant "Nitrokemia", at Füzfö [52] the addition during stabilization boiling of substances capable of swelling nitrostarch is suggested in order to facilitate penetration of the stabilizing liquor into the grains of nitrostarch. Such compounds as epichlorohydrin can act as swelling agents.

For laboratory purposes nitrostarch may be stabilized by boiling with ethyl alcohol. The insoluble part containing 13.4–13.9% N is characterized by considerably higher chemical stability than the raw product before boiling (Ashford, Cook and Hibbert [39]).

NITROCHITIN

Chitin is a long-chain polymer (similar to cellulose) composed of β-N-acetyl glucosamine unit (Meyer and Mark [53]). Every unit contains two OH groups and one $NH–COCH_3$ group:



Nitration of chitin was carried out for the first time by Fürth and Scholl [54]. They tried to produce degradation of the chitin by acting with fuming nitric acid (*d* 1.525). They obtained two products: one insoluble in the common organic solvents, the other soluble in polar solvents. Most likely they were nitrochitin and the oxidation product, respectively. The authors pointed out a similarity between nitrochitin and nitrocellulose. Later on, Schmidt [55] examined the birefringence of chitin and nitrochitin.

The most extensive experiment on nitrochitin preparation and properties were reported by Shorygin and Khait [56]. Shorygin and Khait found that the ordinary nitrating mixture cannot be used to nitrate chitin, as decomposition occurred when the nitrating mixture contained sulphuric acid. They prepared nitrochitin by dissolving chitin in fuming nitric acid (*d* 1.50). After 1–2 hr the solution was poured into large volume of water. The nitrochitin was precipitated in the form of white flakes. The nitrogen content of the ONO_2 groups was 7.5% N, which corresponds to 1.5 ONO_2 groups in every glucosamine unit.

Shorygin and Khait described the properties of nitrochitin. It burns readily when ignited. The ignition temperature is about 163°C. It withstands the heat test at 65°C for 3–8 hr (no change of the colour of starch–potassium iodide paper).

Nitrochitin is partly soluble in formic acid and can be fractionated into two parts by means of this solvent. It can be precipitated with water from the solution in formic acid. The two fractions differ very little with respect to the nitrogen content, but very probably they differ in molecular weight. Nitrochitin swells in benzene, tetralin, nitrobenzene, aniline, phenol, pyridine and furfural.

NITRO-DERIVATIVES OF LIGNIN

An appreciable part of the lignin molecule is aromatic in character. Hence it would be expected to take part readily in the reaction of nitration. It has been found, however, that the capacity of lignin to undergo oxidation predominates especially in the presence of dilute nitric acid. This can be explained by the fact that the aromatic part of the lignin molecule derives from pyrocatechol. The reaction of lignin with nitric acid forms the basis of a method of separating cellulose from wood pulp, that consists in treating this mass with dilute nitric acid (3–10%).

The reaction may be applied in analysis or as an industrial process. Thus Krais [57] obtained patents for producing cellulose from wood pulp by means of 3–6% nitric acid.

The earliest experiments devoted to the nitration of lignin, previously isolated

from wood pulp by means of hydrochloric acid, were carried out by Hägglund [58]. Lignin mixed with fuming nitric acid was heated on a water bath until the lignin was completely dissolved, whereupon the nitration product was precipitated by diluting the solution with water. In the aqueous solution oxalic acid was the main product. Hägglund did not investigate more closely the nitrolignin obtained in this way.

Several authors have examined the effect on lignin of nitric acid or its mixture with sulphuric acid.

Detailed investigations were carried out by Fischer and Schrader [59] who nitrated lignin by treating it with 31.5% nitric acid at room temperature, completing the operation with moderate heating. Only 4.3% of nitrogen was found in the product, to which the formula $C_{39}H_{29}O_{21}N_3(OCH_3)_3$ was assigned on the basis of analysis. At the same time König [60] nitrated lignin at a low temperature in a mixture of nitric acid to obtain a product containing 3% of nitrogen.

Powell and Whittaker [61] nitrated lignin with mixed nitric and sulphuric acid at —5°C. The nitration product was isolated by precipitation with water and ice.

The nitrolignin prepared by these workers was a red powder, with the empirical composition:

$$C_{42}H_{39}O_{13}(NO_2)_3$$

The most extensive investigations devoted to the preparation of nitrolignin by direct nitration of wood pulp were those of Kürschner *et al.* [62]. A solution of nitric acid (*d* 1.40) in ethyl alcohol was used at the temperature of boiling ethanol. Under these conditions cellulose remained unchanged. Lignin, on the other hand, was nitrated and dissolved in the alcoholic solution. Nitrolignin was then separated from the solution by means of water, in the form of an amorphous yellow powder. The yield of nitrolignin was 15–17% of the weight of wood pulp. According to the type of wood used to prepare the lignin the nitrogen content of the fully nitrated product varied from 3.0–4.5%.

On the basis of his own experiments, Kürschner suggested the following functional composition of nitrolignin:

$$C_{18}H_{13}O_2(COOH)(OH)_2(OCH_3)(NO_2)$$

In order to separate lignin from carbohydrates stronger reagents were used in the experiments of Friese *et al.* [63] for the nitration of wood pulp, namely normal mixed acids. In this way nitrolignin with a higher nitrogen content was obtained.

When nitric acid and sulphuric acid mixed in a 1:2 ratio were used a product containing 8.45% N was obtained with a yield of 55%. O-nitro groups make up 7.1% N whereas the contribution of C-nitro groups was only 1.35%. An approximately equal relationship between the C-nitro and O-nitro groups was reported by these investigators on nitrating by means of mixtures consisting of nitric and phosphoric acid or nitric acid, acetic acid and acetic anhydride.

A property of the nitration product of lignin which attracted attention was its failure to form detectable amino groups on reduction. The product of reduction

could not be diazotized. The reason for this phenomenon is still a matter for controversy. However, Kürschner's view [62] that the amino groups produced in consequence of reduction enter into reaction with the carboxyl group to form a lactam ring seems feasible.

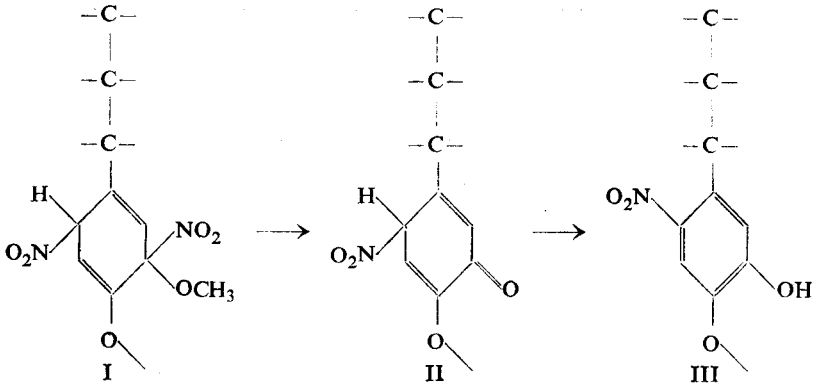
In the course of treating lignin with nitric acid, especially with dilute acid, hydrocyanic acid is evolved. This is explained by the formation of nitrosophenols that undergo a tautomeric conversion into quinone oximes, the latter then being oxidized and hydrolysed. During these reactions HCN is split off in a manner resembling that reported by Seyewetz [64] (compare Vol. I).

In spite of the aromatic character of lignin the experiments described indicate that it is unsuitable for manufacturing nitro compounds likely to be of practical value as explosives.

Nevertheless these experiments have helped to clarify the chemical character of lignin. From this point of view the researches of Freudenberg *et al.* [65], who acted on lignin with nitrogen dioxide or with nitric anhydride are also of importance.

The most noteworthy experiments were these in which nitrogen pentoxide was used in chloroform solution. Thus Freudenberg obtained a product containing 4.7% of nitrogen that corresponds to 0.9 nitro group for a unit comprising one aromatic ring. Freudenberg considered that partial removal of the methoxy groups occurred during nitration. Hence methyl alcohol or methyl nitrite were present among the reaction products.

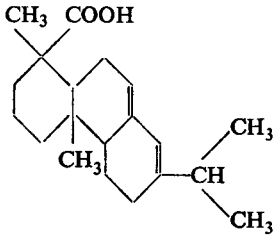
To explain this fact Freudenberg proposed the following reaction scheme:



in which the formula (I) represents the original product of nitration of lignin, while (II) is a semiquinone which is transformed into a nitrophenol (III).

NITRO-DERIVATIVES OF ABIETIC ACID

It is known that the solid residue of distillation of essential oils (turpentine) of coniferous tress—rosin or colophony—is composed mainly of abietic acid:



Nitration of abietic acid was reported in 1904 [66]. Johansson [67] was the first to describe a crystalline nitro-derivative which he considered to be dinitro-abietic acid of the formula $C_{19}H_{27}(NO_2)_2COOH$, m.p. 178–184°C (see also [68]). Later reports by Dubourg [69], Goldblatt *et al.* [70] described the nitration in nitric acid ($d = 1.42$) in presence of acetic acid to form dinitroabietic acid $C_{18}H_{25}(NO_2)_2COOH$ of m.p. 171°C (yield 33%).

Fieser and Campbell [71] nitrated dehydroabietic acid with nitric–sulphuric acid mixtures and obtained a product $C_{19}H_{25}(NO_2)_2COOH$, decomposition 178–185°C, identical with this described by Johansson. This was 6,8-dinitro-dehydroabietic acid. It seems to be identical with one of the non-identified products with three (?) NO_2 groups of Dubourg [69].

A trinitroabietic acid, $C_{15}H_{16}(NO_2)_3COOH$, m. p. 156–158°C, was also obtained by Dubourg. He also prepared polynitroabietic acid by nitration of abietic acid with hot anhydrous nitric acid.

An ethyl ester of dinitroabietic acid (m.p. 157.5–158°C) was also described by Goldblatt *et al.* [70].

Nitro-derivatives of abietic acid did not find any practical application, although a few patents were issued [72].

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CHAPTER XVII

SUGAR NITRATES ("NITROSUGARS")

HISTORICAL

LONG ago, such widely occurring and readily available carbohydrates as glucose, lactose, galactose, and saccharose attracted the attention of chemists, who examined these substances to find out whether they were suitable raw materials for manufacturing explosives, in the form of nitric esters.

However, as the result of investigations carried out during different periods of the nineteenth century it became clear that the nitration of sugars was a very delicate operation. The formation of resinous products can occur with the greatest ease. The residues of the nitrating acid are removable only with difficulty and no economic purification process was available. In consequence the product was unstable and it readily suffered decomposition. It was shown, however, by the extensive studies of Will and Lenze [1], that it is possible to obtain crystalline products from the majority of the sugars examined. The following is a general method of O-nitration of sugars. Sugar is dissolved in nitric acid at a temperature below 0°C, and the solution is then poured into well stirred sulphuric acid, the temperature being kept below 0°C. The corresponding sugar nitrate is precipitated. After being separated from acid by filtration, the product is washed with water and ice and then crystallized, most frequently from alcohol. There exist certain sugar nitrates that have no distinct melting point despite being crystalline merely softening within rather wide temperature limits.

Recently a chromatographic method of purifying sugar nitric esters on aluminium oxide has been described (Ansell and Honeyman [2], Honeyman and Morgan [3]).

The nitration of sugars was also studied by: Hlasiewetz and Pfaundler [4], Lea [5], Colley [6], Elliott [7], Gé [8], E. J. Hoffman and Hawse [9], Pictet *et al.* [10, 11], and a number of authors whose studies are mentioned later. The most noteworthy of the earlier results, mainly those of Will and Lenze [1], are collected in Table 109.

An excellent review on sugar nitrates was given by Honeyman and Morgan [3].

TABLE 109

THE RESULTS OF NITRATING DIFFERENT SUGARS

Type of sugar	Formula and nitration degree	Crystallization solvent	Melting point °C	Stability	
				Loss of weight at 50°C	Temperature of decomposition °C
Monoses					
L-Arabinose	$C_5H_6O(ONO_2)_4$		85	40% after 40 days	120
D-Xylose	$C_5H_6O(ONO_2)_4$		liquid	—	—
D-Xylose	$C_5H_7O_2(ONO_2)_3$		141	—	—
L-Ramnose	$C_6H_8O_2(ONO_2)_4$		135	1.2% after 30 days	—
L-Ramnose	$C_6H_9O_3(ONO_2)_3$		*ca.* 100	—	—
D-Galactose	$C_6H_7O(ONO_2)_5$	ethyl alcohol	α 115–116	42% after 1 day	125
			β 72–73	46% after 1 day	125
D-Glucose	$C_6H_7O(ONO_2)_5$		liquid	38% after 1 day	135
D-Mannose	$C_6H_7O(ONO_2)_5$		81–82	46% after 1 day	124
α-D-Glucoheptose	$C_7H_8O(ONO_2)_6$	ethyl alcohol	100		
Bioses					
Maltose	$C_{12}H_{14}O_3(ONO_2)_8$	methyl alcohol	164–165	23% after 43 days	170–180
Lactose	$C_{12}H_{14}O_3(ONO_2)_8$	methyl or	145–146	40% after 40 days	135
Lactose	$C_{12}H_{16}O_5(ONO_2)_6$	ethyl alcohol	70	—	—
Saccharose	$C_{12}H_{14}O_3(ONO_2)_8$	,,	85	11% after 3 days	135
Trehalose	$C_{12}H_{14}O_3(ONO_2)_8$	methyl or ethyl alcohol	124	—	136
Trioses					
Raffinose	$C_{18}H_{21}O_5(ONO_2)_{11}$		55–65		136

PREPARATION

According to the recent experiments of Fleury, Brissaud and Lhoste [12], the nitration of sugars can be carried out at a temperature of about 0°C by means of a mixture prepared from 2 parts anhydrous nitric acid, 1 part acetic anhydride and 1 part acetic acid. A quantitive yield is thus achieved. Further, crystallization of the products is achieved more easily than with esters obtained by nitration with nitric and sulphuric acid.

The following products were prepared by these authors:

	Melting point, °C	Ignition temperature, °C
(1) D-α-anhydroglucose pentanitrate	53.5	200
(2) D-β-anhydroglucose pentanitrate	111	257
(3) D-α-xylopyranose tetranitrate	73.5	250
(4) β-cellobiose octanitrate	140	287

It is possible to crystallize the majority of these esters from hydrated or anhydrous alcohol. These compounds are not stable. Their weight decreases on heating at 100°C, as follows:

compound (1)	60 parts within 10 hr
compound (2)	60 parts within 6 hr
compound (3)	60 parts within 10 hr
compound (4)	35 parts within 20 hr

Monasterski [13] has carried out experiments on nitration of saccharose by means of a mixture of anhydrous nitric acid and oleum 17%, in the presence of urea nitrate, at a temperature not above +2°C. After washing in water, in sodium carbonate solution, and in water again, the product was crystallized from ether–alcohol. Maltose was also nitrated in the same way.

Will and Lenze [1] reported that monoses, in contact with mixed acid at 0–15°C for a period of two days, yield pentosan and hexosan nitric esters. This probably takes place in consequence of the dehydrating action of such mixture on the monoses.

In this way they obtained:

from D-xylose: xylan dinitrate $C_5H_6O_2(ONO_2)_2$ (m.p. 75–80°C);
D-galactose: galactosan trinitrate, $C_6H_7O_2(ONO_2)_3$;
D-glucose: glucosan trinitrate, $C_6H_7O_2(ONO_2)_3$ (m.p. about 80°C);
D-fructose: fructosan trinitrate $C_6H_7O_2(ONO_2)_3$, in two crystalline forms; α (m.p. 139–140°C, temp. of decomposition 145°C), β (m.p. 48–52°C, temperature of decomposition 135°C)
D-sorbose: sorbosan trinitrate, $C_6H_7O_3(ONO_2)_3$ (m.p. 40–54°C).

Methylglucosides were also nitrated by Will and Lenze [1]. From methyl-α-D-glucoside they obtained the tetranitrate, $C_7H_{10}O_2(ONO_2)_4$, melting at 40–50°C. This is considerably more stable than glucose pentanitrate, its loss of weight after 5 days at 50°C being barely 0.7%. Its decomposition temperature is 135°C.

From methyl-α-D-mannoside a similar product, $C_7H_{10}O_2(ONO_2)_4$, was obtained in the form of needles, melting at 36°C, rather unstable at 50°C.

Fleury, Brissaud and Lhoste [12] also prepared alkyl glucoside esters, using the nitrating mixture described above, composed of nitric acid, acetic anhydride and acetic acid:

(1) methyl-α-D-glucopyranoside tetranitrate (m.p. 48°C) (also Brissaud, Leclercq and Roussin [14]); (2) methyl-β-D-glucopyranoside tetranitrate (m.p. 116.5°C); (3) ethyl-D-xylopyranoside trinitrate, that transforms on crystallization into (4) ethylxyloside trinitrate (m.p. 95.5°C); (5) methyl-β-cellobioside heptanitrate (m.p. 134°C).

The stability of the above compounds is indicated by the following figures that show the loss of weight on keeping the specimen at a temperature of 100°C:

for (1) — the loss is 3% within 20 hr
(2) — the loss is 5% within 20 hr
(4) — the loss is 3% within 20 hr
(5) — the loss is less than 1% during 20 hr.

Besides these investigations which were undertaken to determine whether sugar nitrates were of any practical value as explosives, a series of papers devoted to the theoretical problems of the sugar chemistry have been published. It has been found possible to remove nitrate groups selectively from determined positions by means of methods outlined below, and also to bring about complete denitration by means of reduction processes. These techniques were successfully employed, for instance, in synthesizing a range of new D-glucose, D-galactose, and D-fructose methyl ethers.

The applications mentioned are well illustrated by the following example. Methyl-β-D-glucopyranoside 2,3-dinitrate was converted in the presence of methyl iodide and silver oxide into the 4,6-dimethyl ether of the above nitrate, whereupon it was treated with trityl chloride and acetic anhydride in pyridine eventually yield methyl 4-O-acetyl-6-O-trityl-β-D-glucoside 2,3-dinitrate (Bell and Synge [15]).

Experiments have been made with more moderate nitrating reagents both in order to achieve a more easily controlled reaction than that resulting from the use of a mixed nitric and sulphuric acid, and also with the view to obtaining less impure products. Thus Königs and Knorr [16] used a solution of nitric acid in chloroform to nitrate β-D-glucopyranose penta-acetate, obtaining 2,3,4,6-tetra-O-acetyl-α-D-glucosyl nitrate. Only the acetyl group attached to the C atom was substituted by the nitro group.

Use was also made of a nitric acid solution in chloroform containing phosphorus pentoxide (Oldham [17]). In this way Oldham nitrated trimethyl glucose ether and triacetyl-1,6-anhydroglucopyranose and obtained the crystalline substances: 2,3,5-trimethyl-α-D-glucose 1,6-dinitrate (m.p. 86°C), triacetyl-α-D-glucose 1,6-dinitrate (m.p. 132–135°C).

Nitrogen pentoxide dissolved in chloroform is an excellent O-nitrating agent (Oldham [17]). Montgomery and Clark [18] obtained 1,2,4,5-di-O-isopropylidene-D-fructose 3-nitrate in that way. According to Bell and Synge [15] below 0°C methyl-4,6-O-ethylidene-β-D-glucoside was transformed mainly into 2,3-dinitrate within about 5 min.

With nitric acid, methyl β-D-glucoside 2,3,4,6-tetranitrate is the chief product, probably due to the stronger hydrolysing power of nitric acid, which causes the labile acetal system to break down.

Methyl 4,4-O-benzylidene-α-D-glucoside was converted by Honeyman and Morgan [3] into its 2,3-dinitrate; neither its acetal system nor the aromatic ring was nitrated.

By treating 2,3,4,6-tetra-O-acetyl-α-D-glucosyl chloride in ether solution with silver nitrate (Schlubach, Stadtler, Wolf [19]) 2,3,4,6-O-acetyl-α-D-glucosyl nitrate was obtained.

Leibowitz and Silmann [26] have nitrated the degradation products of poly-amylose, namely "di-, tri-, and tetra-amylose". Following in principle the nitration method introduced by Will and Lenze, Leibowitz and Silmann obtained a series of compounds, which they named:

α-diamylose hexanitrate, $[C_6H_7O_2(ONO_2)_3]_2$, m.p. 206°C, crystallized from acetic acid;
β-triamylose hexanitrate, $[C_6H_8O_3(ONO_2)_2]_3$, m.p. 203°C, crystallized from ethanol;
β-triamylose nonanitrate, $[C_6H_7O_2(ONO_2)_3]_3$, m.p. 198°C, crystallized from acetic acid;
α-tetra-amylose octanitrate $[C_6H_8O_3(ONO_2)_2]_4$, m.p. 204°C, crystallized from acetic acid.

All the products were unstable, as within several months of storing in a desiccator, a loss of weight of some 75% was noted.

CHEMICAL PROPERTIES

Fehling's solution is reduced at an elevated temperature by all sugar esters including esters of bioses and trioses.

Sugar nitric acid esters are also subject to reductive denitration (see p. 9) and to the chemical reactions typical of sugar nitrates.

One of these consists in the substitution of iodine for the ester group attached to the primary carbon atom as the result of prolonged heating with sodium iodide in acetone solution (Finkelstein's reagent (20]). The reaction appears likely to consist in breaking the C—O linkage:

$$-CH_2-ONO_2 + NaI \longrightarrow -CH_2I + NaNO_2 \qquad (1)$$

Finkelstein's reagent was first brought into use for this purpose by Oldham [17]. The secondary ester radical does not undergo this chemical reaction, but it may suffer hydrolysis followed by the formation of an OH group:

$$\rangle CHONO_2 \xrightarrow{NaI} \rangle CH-OH \qquad (2)$$

Such a reaction takes place more or less readily depending on the position of the atom to which the hydroxyl group is attached. Thus, Oldham and Rutherford [21] kept methyl-2,3-di-O-methyl-β-D-glucoside and sodium iodide in acetone at 100°C for 20 hr and obtained methyl 6-desoxy-6-iodo-2,3-di-O-methyl-β-D-glucoside, accompanied by a small amount of 4-nitrate. As for the β-D-gluco-pyranoside tetranitrate, it seems that the nitrate group attached to the C_4-carbon atom is more reactive than the C_3-nitrate. Thus, Honeyman and Morgan [3] reported that methyl 4,6-O-ethylidene-β-D-glucoside 2,3-dinitrate, exposed to heating with NaI under the same conditions as above (20 hr at 100°C) produced the 3-nitrate with a good yield.

The reaction mechanism seems likely to be different when secondary ester is hydrolysed by means of sodium iodide. It appears to consist in breakage of the O—N bond:

$$\rangle CH-O-NO_2 + NaI \longrightarrow \rangle CH-O-Na + NO_2I \qquad (3)$$

$$NO_2I + NaI \longrightarrow NaNO_2 + I_2 \qquad (4)$$

Among other characteristic chemical reactions of the sugar nitrates, the reaction with sodium nitrite ethanol solution deserves attention. It is used to remove

an NO_2 group from a secondary ester. Thus methyl-4,6-O-ethylidene-α-D-glucoside and 4,6-O-benzylidene-α-D-glucosyl 2,3-dinitrate are converted after about 12 hr of boiling into the corresponding 3-nitrate. The primary ester groups undergo this interchange only in particular cases.

Pyridine and hydroxylamine separately exert only a weak influence on the high-nitrated sugar esters of nitric acid, whereas when they are used together they bring about somewhat violent chemical reaction, as demonstrated by Hayward and Purves [21a].

In this way, from methyl-α-D-glucopyranoside tetranitrate a mixture composed of lower nitrated esters, mainly 2,3,6-trinitrate (28% yield), and 3,6-dinitrate (17% yield) is formed. This is also the best way of any to remove the nitrate group attached to the C_4-carbon atom.

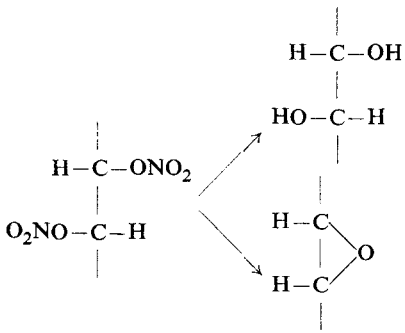
The alkaline hydrolysis of nitric esters can furnish a complicated mixture o products as formerly described (p. 7).

Owing to the ability of alkalis to attack carbonyl compounds, however, clearly the products obtained by the hydrolysis of sugars are more complicated than those obtained from simple nitric esters. This was described in detail by Honeyman and Morgan [3]. It should be pointed out that relatively mild alkaline agents, such as barium carbonate in boiling methanol can also be used to hydrolyse the nitrate groups, e.g. 2,3,4-tri-O-methyl-α-D-glucose 1,6-dinitrate is converted into the corresponding tri-O-methyl-α-D-glucopyranoside.

A high yield of methyl 3,6-anhydro-α-D-glucopyranoside was obtained on treating methyl α-D-glucopyranoside-6-nitrate with alkali (Gladding and Purves [22]).

Investigations by Honeyman [3] have shown that two modes of heterolytic fission of 2,3-nitrate groups can occur under the action of sodium methoxide in methanol on 4,6-O-benzylidene-α-D-glucoside 2,3-nitrate.

A small yield of 7.5% of 2,3-anhydro-α-D-alloside-3-nitrate, and methyl 4,6-O-benzylidene-α-D-glucoside was obtained. The formation of two last products could be explained by the diagram:



(5a)

(5b)

2,3-anhydro-α-D-alloside

Anbar, Dostrovsky, Samuel and Yoffe [23] confirmed the existence of these two modes of fission by the use of a solution of alkali in water containing ^{18}O.

EXPLOSIVE PROPERTIES

The explosive properties of nitrosugars have been examined by Monasterski [13]. This author reported that saccharose octanitrate developed a heat of explosion of 950 kcal/kg, and produced in the lead block an expansion of about 300 cm^3. In the drop test it exploded from the impact of a 2-kg weight falling from a height of at least 20 cm. Maltose octanitrate, in the lead block, caused a net expansion of some 260 cm^3.

Médard [23a] examined the explosive properties of methyl-α-D-glucopyranoside tetranitrate prepared according to Fleury *et al.* [12]. The product requires a relatively weak initiator, e.g. 0.25 g of mercury fulminate suffised to detonate a sample of the substance of density 1.10. Only the cast product (density 1.65) requires a strong detonator (over 1.5 g fulminate).

The sensitiveness to impact is expressed by the data: 50% explosions were obtained by the impact of 1 kg from the height of *ca.* 105 cm. The data are similar to those of cyclonite.

The relative lead block expansion was found to be 130 (picric acid = 100), and the rates of detonation of charges of 30 mm dia. in cardboard tubes were:

density 1.10	5630 m/sec
density 1.50	6970 m/sec
density 1.60	7560 m/sec.

Cast charges (density 1.65) of 20 mm dia. gave the rate of 7830 m/sec.

Médard concluded that methyl-α-D-glucopyranoside tetranitrate is only slightly inferior to cyclonite with regard to its explosive power. Médard also examined mixtures of the substance with dinitrotoluene or ammonium nitrate.

Practical application has been achieved only in the U.S.A. where a mixture of nitrated saccharose with nitroglycerine has found some use. In order to produce such an explosive, a mixture containing 20–25% of saccharose and 75–80% of glycerine is nitrated to produce an oily nitration product [24]. This material was used for the manufacture of dynamite instead of pure nitroglycerine. A mixture of this kind was commercially produced in U.S.A. on economic grounds, namely saccharose was cheaper than glycerine [25].

The product of nitrating saccharose mixed with glycerine marketed under the trade name *Nitrohydrene*, has an appreciably higher viscosity than nitroglycerine itself, hence its stabilization washing is considerably more difficult. Nitrohydrene is particularly inclined to form a water emulsion. To cause it to separate more completely from water after being washed in sodium carbonate solution Nitrohydrene is treated with a sodium chloride solution. The composition of Nitrohydrene differs slightly from that of the original mixture. Nitrohydrene 80/20 obtained by nitrating a mixture consisting of 80% of glycerine and 20% of saccharose contains 86% of nitroglycerine and 14% of nitrosaccharose. In Nitrohydrene 75/25, 82% of nitroglycerine and 18% of nitrosaccharose are present.

The stability of Nitrohydrene is significantly worse than that of nitroglycerine.

The higher the nitrosaccharose percentage in the mixture, the lower its stability. According to Naoúm [25] wood meal admixed with dynamite may act as a stabilizer, because it absorbs the impurities or the decomposition products and can enter into reaction with these compounds, thus removing them. With the aim of improving storage life, 0.1–0.2% of diphenylamine is also added to act as a stabilizer. A mixture prepared in this way can be kept for 75 days at 55°C or for 8 years at 20°C with no sign of decomposition.

Naoúm [25] has determined the values of the lead block expansion as follows:

Nitroglycerine	550 cm^3
Nitrohydrene 80/20	530 cm^3
Nitrohydrene 75/25	515 cm^3

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CHAPTER XVIII

ESTERS OF OXY-ACIDS OF CHLORINE

ESTERS of hypochlorous, chloric and perchloric acid possess explosive properties, but due to their extraordinary sensitiveness to friction, to impact or even to shaking, they have not found any practical application.

Ethyl hypochlorite, C_2H_5OCl, is a substance that is decomposed with explosion when irradiated by sun-light or brought into contact with copper dust. Methyl hypochlorite, boiling at 12°C, also exhibits similar properties.

Ethyl hypochlorite is a yellow liquid, the boiling point of which is 36°C (Sandmeyer [1]). It was prepared by introducing chlorine gas into a cooled mixture composed of 1 part of sodium hydroxide, 1 part of ethanol and 9 parts of water.

Ethyl perchlorate, $C_2H_5OClO_3$, was first prepared by Hare and Boyle [2] as early as 1841. These authors drew attention to the highly explosive character of the substance and the danger of handling it. It is an oil liable to explode even when it is poured from one vessel into another. They obtained it by digesting barium ethyl sulphate with barium perchlorate. Later it was prepared by Roscoe [3] by acting with silver perchlorate on ethyl iodide.

Methyl perchlorate exhibits similar properties.

The explosive properties of these two substances were examined by Berthelot [4]. He found that methyl perchlorate is endothermic substance, with a heat of formation $-\Delta H_f$ of 4 kcal/mole.

The explosive decomposition of methyl perchlorate approximately follows the equation:

$$CH_3ClO_4 \longrightarrow CO_2 + H_2O + HCl + \tfrac{1}{2}O_2 + 1529 \text{ kcal/kg}$$

the volume of gases produced (V_o) is 713 l./kg. These data approximate closely to the corresponding values for nitroglycerine.

It has been found possible (K. A. Hofmann and Zedtwitz [5]) to obtain the esters of perchloric acid by treating alcohols with nitrosyl perchlorate, $NO \cdot ClO_4 \cdot H_2O$. Nitrosyl perchlorate is a stable, crystalline substance that reacts explosively on contact with aromatic amines. In the presence of alcohol the perchlorate and alkyl nitrite are produced.

J. Meyer and Spormann [6] prepared methyl, ethyl and propyl perchlorates from barium ethyl sulphate and barium perchlorate. Their products were oily

liquids very sensitive to heat, impact and friction. They determined the boiling points of methyl and ethyl esters as *ca.* 52 and *ca.* 89°C, respectively.

They also found that methyl perchlorate can be formed by the action of diazomethane on perchloric acid. The esters can be hydrolysed by water. The ease of hydrolysis increases from the propyl to the methyl derivative.

Recently, Radell, Connolly and Raymond [7] prepared normal pentyl, hexyl, heptyl and octyl perchlorates from the corresponding alkyl iodide and silver perchlorate. The oily esters were purified as urea inclusion compounds.
Their boiling points were:

$n\text{-}C_5H_{11}OClO_3$	51.5°C (11 mm Hg)
$n\text{-}C_6H_{13}OClO_3$	52.0°C (4.5 mm Hg)
$n\text{-}C_7H_{15}OClO_3$	49–51°C (2.5 mm Hg)
$n\text{-}C_8H_{17}OClO_3$	55–60°C (1.5 mm Hg)

The authors examined the infra-red spectra and found a number of characteristic bands:

Cl—O asymmetric stretching 1260, 1230 cm^{-1}
Cl—O symmetric stretching 1035 cm^{-1}
Cl—O stretching 1125–1080, 709–704 cm^{-1}.

Their sensitiveness to impact varies from 5 to 12.7 cm (5-kg weight) and decreases with an increase of the molecular weight. The ignition temperature varies from 150°C (n-pentyl perchlorate) to 350°C (n-octyl perchlorate).

K. A. Hofmann, Zedtwitz and Wagner [8] also obtained the esters listed below:
diethylene glycol monoperchlorate, $ClO_4 \cdot C_2H_4OC_2H_4OH$ (I)
chlorohydrin monoperchlorate, $ClO_4 \cdot CH \cdot {}_2CHOH \cdot CH_2Cl$ (II)

The substance (I) was obtained by treating ethylene oxide with 60% perchloric acid, and the compound (II) by acting with 60% perchloric acid on epichlorohydrin.

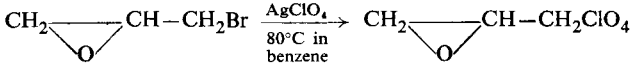
The physical state of both esters is that of an oil immiscible with water. According to these investigators, the compounds are strong explosives producing an explosive effect larger than nitroglycerine. Under the influence of water at the room temperature or directly in the presence of atmospheric moisture, the perchlorates are readily hydrolysed, hence their importance in practice is negligible. The stability of the compound (I) is considerably higher than that of (II). Even so it is insufficient to make it practicable to use substance commercially.

Zinovyev *et al.* [9] prepared partial or complete esters with ethylene glycol, glycerine and pentaerythritol by setpwise addition of the alcohol to be nitrated to anhydrous perchloric acid at —75 to —78°C, followed by heating to 60 to 80°C. The reaction mixtures could not be diluted with water since even a few drops of water caused violent explosion. Dilution was effected by adding the constant boiling mixture of perchloric acid and water after which water was added to separate the heavy esters. The esters were extracted with ether. Separation of the ether layer could not be carried out in ordinary funnels as an explosion can occur when the solution enters a ground glass stop-cock. All the products were oily liquids,

except the pentaerythritol esters, which were solids. All the perchlorates were very sensitive to impact and friction, and exploded even on careful pouring from one container to another.

A number of alkaryl perchlorates were also prepared for analytical purposes [10].

An interesting attempt to prepare a perchlorate polymer was made by Radell and Connolly [11]. They prepared epiperchloratohydrin (I) from epibromohydrin:



I

The product (I) polymerized on standing to yield a viscous, sirupy mass. It was unstable and exploded at a temperature as low as 25°C after the solvent was removed.

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CHAPTER XIX

SALTS OF NITRIC ACID

THE salts of nitric acid can be divided into two groups: explosive and non-explosive. Metallic salts, e.g. sodium nitrate, potassium nitrate are not explosives themselves. None the less use is made of them in many explosive mixtures, as components that act as readily available oxygen carriers.

There are also salts of nitric acid that demonstrate explosive properties. This group consists both of inorganic nitrates such as ammonium nitrate, and of organic nitrates. Despite their marked explosive properties these substances are usually used only as ingredients of explosive mixtures.

AMMONIUM NITRATE

Ammonium nitrate is the most readily available and cheapest salt of nitric acid, now manufactured wholly from synthetic ammonia and from nitric acid obtained by oxidation of ammonia. Ammonium nitrate was prepared for the first time as early as in 1659 by Glauber. The original experiments with it as a component of explosive mixtures began in the second half of the nineteenth century. Ammonium nitrate is the most widely used oxygen carrier, since it is an ingredient of the commonest group of high explosives. The reasons for this are to be seen in its properties and those of its explosive mixtures: appreciable chemical stability, and low sensitiveness to friction and to shock.

The disadvantage of ammonium nitrate, which limits its application, is its hygroscopicity.

PHYSICAL PROPERTIES

Ammonium nitrate exists in the form of crystals, melting at 169.6°C. It occurs under five crystalline modifications distinguished by the transition temperatures:

$$\text{Tetragonal } \alpha\text{ (V)} \xrightleftharpoons{-18^\circ\text{C}} \text{Orthorhombic } \beta\text{ (IV)} \xrightleftharpoons{+32.1^\circ} \text{Orthorhombic } \gamma\text{ (III)} \xrightleftharpoons{84.2^\circ\text{C}}$$

$$\rightleftharpoons \text{Tetragonal } \delta\text{ (II)} \xrightleftharpoons{125.2^\circ\text{C}} \text{Cubic } \varepsilon\text{ (I)} \xrightleftharpoons{169.6^\circ\text{C}} \text{Liquid}$$

Attention was first drawn to the existence of several crystalline variations of ammonium nitrate by Frankenheim in 1854 [1].

At temperatures above 169°C, under pressures exceeding 9000 kg/cm^2, Bridgman [2] has established the existence of one more form (VI).

The experiments of Volfkovich, Rubinchik and Kozhin [3] indicated that only three transformations are observed when melted ammonium nitrate is cooled quickly at 2°C per minute:

$$\text{Liquid state} \xrightarrow{169°C} \text{(I)} \xrightarrow{125°C} \text{(II)} \xrightarrow{50°C} \text{(IV)}$$

Owing to rapid cooling, form (II) changes directly to form (IV) at 50°C, omitting the transitions that would take place at 84.2 and 32.1°C. An indispensable condition for this behaviour consists in cooling the liquid phase. The phenomenon has not been observed on cooling ammonium nitrate previously heated to 125°C, because the formation of the form (III) is clearly noticeable here. Likewise the transformation at 50°C does not occur when the variation (IV) is heated, as in this case forms (III) and (IV) develop in turn.

The same authors also detected that cooling the form (V) below —170°C causes further transformation to a modification which the authors suggest should be designated as (VII).

The transition at the temperature of 32.1°C, or according to some authors at 32.3°C, from the orthorhombic β-form into the γ-form is accompanied by a volume increase of the crystals of *ca.* 3%. Simultaneously the crystals are split into smaller ones. When the γ-form is cooled, its smaller crystals tend to agglomerate (to "cake"). If moisture is present in the salt, lumps are formed. Both the phenomenon itself and methods of preventing it are discussed more widely later.

The specific gravity of the orthorhombic β-modification is 1.72, and that of the γ-form is 1.66. On heating the substance above 84.2°C a convertion into the δ-variation, followed by an increase of the sp. gr. up to 1.69, occurs.

A negative thermal effect accompanies the transformations of the ammonium nitrate crystal form with rising temperature, whereas during cooling the process is of course exothermic (Table 110).

The transformations, particularly at the temperatures of 32.1 and 84.2°C, are very important with reference to the manufacture and application of ammonium nitrate explosives. In the manufacture of mining explosives containing ammonium nitrate care should be taken that the cartridges are filled with material cooled below 32.1°C. Likewise the temperature inside the various storage rooms in transit during production as well as in the storehouse of finished explosives, should not be allowed to rise above 30°C. Neglecting to observe these conditions may cause the cartridges to harden (see Vol. III). Further, it should be taken into consideration that as the result of loading shells with hot amatols or with any other explosive material containing ammonium nitrate, the loading density will change not only in consequence of cooling but also owing to the transformations of the ammonium nitrate crystal forms.

TABLE 110

THE EFFECTS OF TRANSFORMATION BETWEEN AMMONIUM NITRATE CRYSTALLINE MODIFICATIONS (AFTER HENDRICKS, POSNJAK, KRACEK; [3a])

Crystalline form of ammonium nitrate	Temperature °C	Change of volume cm^3/g	Thermal effect cal/g
I → II	125.2	−0.013	+11.9
II → III	84.2	+0.008	+5.3
III → IV	32.1	−0.002	+5.0
IV → V	−18	+0.016	+1.6

C. C. Stephenson, Bentz and D. A. Stevenson [4] have estimated the specific heat of ammonium nitrate at different temperatures from 15 to 315°K. A selection of figures determined by these authors is collected in the table below:

	T, °K	C_p,cal/mole °K
form (V)	15.12	0.43
	33.08	3.39
	73.62	10.74
	132.78	18.01
	175.58	22.55
	216.70	27.00
	250.69	30.62
	252.78	30.91
	254.30	31.13
form (IV)	256.80	31.46
	260.27	30.03
	267.70	30.76
	274.91	31.40
	278.92	31.88
	280.35	31.87
	289.53	32.58
	300.85	33.47
	302.83	33.65
form (III)	308.9	28.63
	311.24	28.78
	313.52	28.85
	314.06	28.87

The changes in specific heat brought about by the conversion from one crystal form into another, particularly by the transition of the form (IV) into the variation (III), are worth noting.

The solubility of ammonium nitrate in water is very high, as shown in Table 111.

TABLE 111

SOLUBILITY OF AMMONIUM NITRATE IN WATER

Temperature °C	Solubility %	Temperature °C	Solubility %
20	66.1	100	91.0
40	73.3	120	94.7
60	80.2	140	97.4
80	85.9	160	99.4

Ammonium nitrate is also soluble in methyl alcohol and ethyl alcohol. In methyl alcohol 14% of ammonium nitrate is dissolved at 18.5°C.

Ammonium nitrate is also miscible with fused salts of nitric acid. The composition of the eutectics and the fusion temperatures of mixtures with sodium, potassium, and calcium nitrate are considered in future chapters (Vol. III). Data concerning the properties of mixtures with guanidine nitrate, nitroguanidine, ethylene diamine dinitrate, are also reported in Vol. III.

Ammonium nitrate is highly hygroscopic: it becomes liquid in moist air.

According to the relative humidity and the temperature, transformation processes changing the crystallographic form of ammonium nitrate or of its mixtures take place, as a result of which the salt may agglomerate into a stiff mass. This is very undesirable and troublesome. Attempts to break up the caked ammonium nitrate by detonation with explosives have caused accident for which the "caking" was indirectly responsible (p. 454). Numerous experiments have been carried out in search of a method to protect ammonium nitrate against caking during storage. Here are the most important proposals which have been made:

(1) Protection of ammonium nitrate against moisture by storage under completely dry conditions, e.g. by means of suitable water-proof packaging, e.g. waxed paper.

(2) Addition of water-absorbing substances, e.g. anhydrous salts that readily form hydrates, such as anhydrous copper sulphate.

The addition of fine-powdered "inert coating" substances which are adhering to the surface of the ammonium nitrate crystals or granules and are simultaneously capable of absorbing moisture, e.g. powdered kaolin, chalk, kieselguhr, silica gel, zinc carbonate or zinc oxide, in amounts from 0.1 to 5%. This method seems to be accepted in many countries.

In France 1% of calcium stearate is added. It is believed to endow ammonium nitrate with a higher resistance against moisture.

Another method was suggested by J. Taylor and Sillitto [5]. It consists in adding of 0.2–1.5% carboxymethylcellulose and calcium stearate to ammonium nitrate. The mechanism of the action of these compounds is based on the fact that carboxymethylcellulose gels rapidly when it comes into contact with water, forming a bar-

rier to the further penetration of water into the composition. Calcium stearate is a substance very difficult to wet with water and so helps water proofing by slowing down the initial wetting. Subsequently it requires more time for the sodium carboxymethyl-cellulose to swell.

(3) Addition of 2–10% fuel oils, generally 4–6%. However, it should to be pointed out that the presence of a relatively large quantity of a combustible material increases the ability of ammonium nitrate to detonate. This is discussed later (p. 461).

(4) Manufacturing granulated ammonium nitrate with granules as uniform in size as possible, in order to prevent the product from containing any powder which would absorb moisture more readily. A fall in humidity owing to the influence of a higher temperature could cause the fine-crushed product to agglomerate. The same result can be obtained by producing ammonium nitrate in the form of minute balls or pellets ("prilled" ammonium nitrate). This shape minimizes the contact surface of the granules whereas any saturated solution of salt is spread over a larger surface, due to surface tension (Dubovitskii [6]).

Adding "inert coating" and fuel oil to ammonium nitrate is more efficient when the latter is in granulated, prilled or flaked form.

(5) Adding to ammonium nitrate small quantities of Acid Magenta, a trisulpho-triamine-methyl-triphenylmethane dyestuff*. According to Butchart and Whetstone [7] 0.1% of this dyestuff admixed with a saturated ammonium nitrate solution or 0.03% of the dye added to the crystals forms an effective layer that prevents ammonium nitrate from caking within the temperature range −18 to 32°C.

The presence of such a small quantity of an organic substance in ammonium nitrate does not increase its sensitiveness to initiators, hence the danger of storing, or transporting these materials is not increased.

(6) In order to prevent caking some authors have suggested avoiding drying at elevated temperatures. Thus Perelman and Klevke [8] suggested drying ammonium nitrate under reduced pressure at temperatures below 0°C.

(7) According to investigations by Jaenecke *et al.* [9] addition of potassium nitrate to ammonium nitrate prevented the transition from modification (IV) into (III) and the change of volume of the ammonium nitrate crystals. Accordingly, it was suggested at the time of World War II that addition of potassium nitrate

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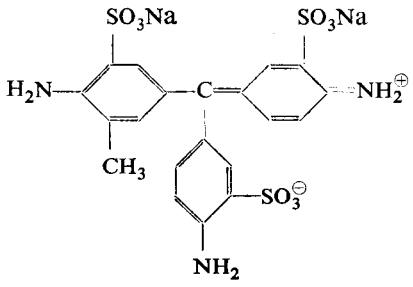


should counteract cracking of compressed or cast charges and agglomeration of powdered ones containing ammonium nitrate.

CHEMICAL AND EXPLOSIVE PROPERTIES

Attention was paid to the explosive properties of ammonium nitrate as early as 1883 by Berthelot [10] who first formulated the equation of decomposition, and gave the numerical data for the heat of explosion, heat of formation, the volume of gases evolved and the temperature of explosion.

Complete detonation of ammonium nitrate is defined by the eqn. (1). Formulae (2), (3), and (4) correspond with incomplete explosion. In a more recent publication Saunders [11] reports that the decomposition of ammonium nitrate at the time of explosion proceeds in accordance with the eqn. (5).

$$NH_4NO_3 \longrightarrow N_2 + 2H_2O + \tfrac{1}{2}O_2 + 346.5 \text{ kcal/kg} \quad (1)$$

$$4NH_4NO_3 \longrightarrow 3N_2 + 2NO_2 + 8H_2O + 300 \text{ kcal/kg} \quad (2)$$

$$NH_4NO_3 \longrightarrow \tfrac{1}{2}N_2 + NO + 2H_2O + 140 \text{ kcal/kg} \quad (3)$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O + 133.6 \text{ kcal/kg} \quad (4)$$

$$8NH_4NO_3 \longrightarrow 5N_2 + 4NO + 2NO_2 + 16H_2O + 132.6 \text{ kcal/kg} \quad (5)$$

Other formulae of decomposition are also possible. Heat of formation $-\Delta H_f$ is 88,6 kcal/mole.

Thermal decomposition. According to A. J. B. Robertson [12] a very high activation energy, $E = 40.5$ kcal/mole, characterizes the thermal decomposition of ammonium nitrate.

Wood and Wise [13] examined the rate of decomposition of ammonium nitrate enclosed in sealed ampoules and kept at temperatures between 200 and 300°C. They found the energy of activation $E = 31.4$ kcal/mole.

Cook and A. Taylor [14] as well as Guiochon and L. Jacqué [15] used a thermogravimetric method to study the decomposition of ammonium nitrate between the temperatures: 217–267 and 180–280°C respectively. They found the energy of activation was 38.3 and 36.5 kcal/mole respectively.

Using the numerical data of Shah and Oza [16], Guiochon [17] also calculated the energy of activation $E = 39.0$ kcal/mole, thus approaching the data of A. J. B. Robertson, Cook and A. Taylor, Guiochon and L. Jacqué. Moreover, all these authors agree that the reaction of thermal decomposition ("thermolysis" according to Guiochon and L. Jacqué) of ammonium nitrate is of the first order (under the conditions studied).

However, Feick and Hainer [18] consider most of the above figures of the energy of activation are not very accurate as in the period prior to explosion a considerable quantity of ammonium nitrate is evaporated. The authors suggest the following equations for ammonium nitrate thermal decomposition:

$$\text{at } 170°C,\ NH_4NO_3 \rightleftarrows NH_3 + HNO_3,\ \Delta H = 35.4 \text{ kcal/mole} \quad (6)$$

$$\text{at } 290°C,\ NH_4NO_3 \rightleftarrows N_2O + 2H_2O,\ \Delta H = -16.4 \text{ kcal/mole} \quad (4)$$

Decomposition accompanied by the development of nitrous oxide compatible with the scheme (4) only starts above 170° C. Marked decomposition together with the evolution of nitrogen, nitric oxide and water, corresponding with the reaction (3), begins at a temperature of about 220°C [11].

Kummer [19], Friedman and Biegeleisen [20] studied the decomposition of ammonium nitrate labelled with ^{15}N: $[^{15}N]H_4$ $[^{14}N]O_3$. The completely anhydrous salt did not decompose until 300°C. Only sublimation took place. But a trace of water initiated decomposition at 180°C. The main products of the reaction were N_2O and water (according to the eqn. (4)) and with the labelled salt, nitrous oxide $[^{14}N]$ $[^{15}N]O$ was produced showing that the gas was formed by the interaction of the two ions in the molecule. They also showed that with ordinary ammonium nitrate and $H_2{}^{18}O$, no $N_2{}^{18}O$ was formed, indicating that the water had a purely catalytic effect.

According to Guiochon [17] the experiments with labelled nitrogen atoms seem to support an earlier suggestion of Davis and Abrams [21] that the decomposition of ammonium nitrate may pass through the intermediate formation of nitramide through dehydration of ammonium nitrate in the first stage (7):

$$NH_4NO_3 \longrightarrow NH_2NO_2 + H_2O \tag{7}$$

$$NH_2NO_2 \longrightarrow N_2O + H_2O \tag{8}$$

The reaction (8) would be very rapid and the reaction (7) is the rate determining step.

A number of authors also examined the influence of addition of various compounds on the thermolysis of NH_4NO_3. Saunders [11], Tramm and Velde [22], Keenan [23] were among those who investigated the influence of the presence of ammonium chloride. The widest experiments on this line were carried out by Guiochon and L. Jacqué [24, 17]. Using the thermogravimetric method, they examined decomposition of ammonium nitrate with ammonium fluoride, chloride, bromide, iodide and sodium chloride between 160 and 250°C. Figure 170 shows the change in weight of the samples of ammonium nitrate — pure and with ammonium chloride: at 200 and 250°C with 5% NH_4Cl and with 0.01, 0.2, 1.0 and 5.0% NH_4Cl respectively.

The authors drew attention to the induction period noticeable in both types of samples: of pure ammonium nitrate and those with ammonium chloride. The time, length and character of the induction period does not seem to depend on the concentration of ammonium chloride in the samples. After the induction period the decomposition of ammonium nitrate with ammonium chloride becomes faster than that of the pure substance. Guiochon and L. Jacqué found that the samples became acid during the induction period. Free nitric acid, and in the samples with ammonium chloride free hydrochloric acid (and subsequently chlorine) are formed. By adding nitric acid or chlorine to the samples, a considerable reduction or suppression of the induction period was achieved.

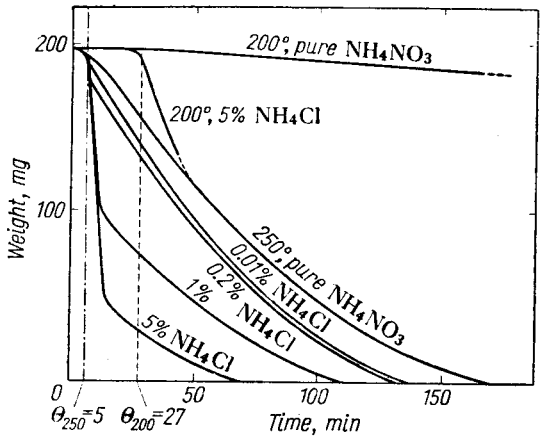


FIG. 170. Thermal decomposition of ammonium nitrate (pure and with varying quantities of ammonium chloride) at 200°C (broken line) and 250°C. Θ—induction period in min, according to Guiochon and Jacqué.

Several authors noticed that the addition of chromium salts to ammonium nitrate increases the rate of its decomposition: Audrieth and M. T. Schmidt [25], Blinov [26], J. Taylor and Sillitto [5], J. Taylor and Whetstone [27], A. J. B. Robertson [12], Shidlovskii [28], Shirai and Ishibashi [29].

J. Taylor and Sillitto found that ammonium nitrate mixed with 3% of potassium chromate or bichromate undergoes spontaneous decomposition ("burning") on being heated to about 400°C. J. Taylor *et al.* [5, 27] suggest utilizing mixtures made from ammonium nitrate and potassium chromate as the main component of rocket solid fuels. This is described in more detail in Vol. III.

The most extensive investigation was carried out by Guiochon and L. Jacqué [30] and Guiochon [17, 31]. They used the same thermogravimetric method as in their former experiments, and examined the influence of chromium oxide (0.3–8%), potassium bichromate (0.1–3%), chromium nitrate (1–5%) and also pure chromium (0.033–5.5%) [30].

The increase in the rate of decomposition under the influence of added Cr_2O_3 and $K_2Cr_2O_7$ is shown on Figs. 171 and 172 respectively. It has been found that an increase of the rate occurred only at temperatures near to the melting point of the samples. Guiochon [17] also found that cobalt salts increase the rate of thermolysis of ammonium nitrate. Other mineral salts (of manganese, nickel and copper) have a similar but much weaker action. A large number of salts of other metals are without any noticeable action.

Thermal decomposition of ammonium nitrate can also be facilitated by adding organic compounds. Thus, ammonium nitrate mixed with cellulose begins to decompose at 100°C and decomposition becomes distinctly perceptible at 120°C. Also salts of some organic bases (e.g. pyridine nitrate) considerably lower the temperature of decomposition of ammonium nitrate.

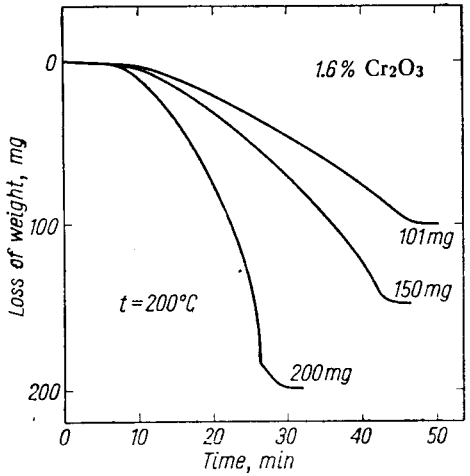


FIG. 171. Decomposition of ammonium nitrate with 1.6% Cr_2O_3 added, according to Guiochon and Jacqué.

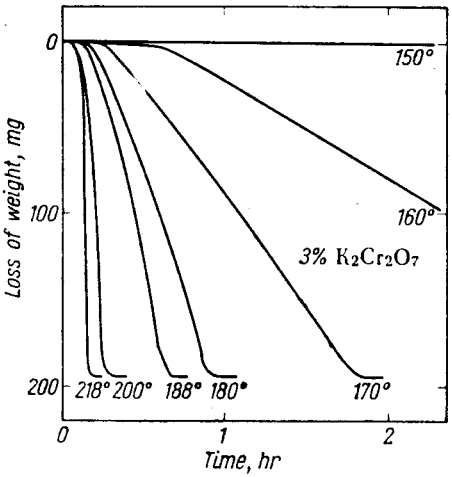


FIG. 172. Decomposition of ammonium nitrate with 3.0% $K_2Cr_2O_7$, according to Guiochon and Jacqué.

Explosive decomposition and stability. The following data are reported to be correlated with the decomposition according to eqn. (1):

volume of gases, V_0	980 l.
temperature,	$t=1500°C$ (Muraour and Aunis [32] found a temperature of 1125°C)
"force",	$f=6570$ m

It has long been realized that ammonium nitrate is one of the most difficult explosive materials to detonate. Moreover, it was generally accepted that it would

be impossible to cause the substance to detonate even by means of exceptionally strong initiation, provided no admixtures of other explosives were present. This view led to the belief that ammonium nitrate was so safe to handle that it was subjected to operations normally permitted only for non-explosive substances. This resulted in several great catastrophes noteworthy in the history of ammonium nitrate manufacture.

In Upper Silesia, in the summer of 1921, while unloading caked ammonium nitrate from a railway car in order to make the work easier shot holes were bored in the material, and charged with an ammonium nitrate explosive, whereupon the charges were exploded. The detonation of these charges was followed by the detonation of ammonium nitrate contained in the car. The detonation was transmitted to ammonium nitrate in the neighbouring car. This accident claimed numerous victims and was accompanied by appreciable material damage.

The largest catastrophe in the history of the chemical industry took place in September, 1921, at Oppau, where a partial detonation of about 4000 tons of a double salt, composed of more or less equal amounts of ammonium nitrate and ammonium sulphate occurred. The cause of this explosion has never been fully explained. Most likely it was brought about by attempts to break up the agglomerated double salt by means of an explosive. Approximately 1000 men were killed in the Oppau explosion.

These catastrophic accidents showed that ammonium nitrate even diluted by another ammonium salt, is an explosive capable of detonating under a sufficiently powerful explosive stimulus [33].

Ammonium nitrate is stable at room temperature, though on storage a little ammonia is evolved, in accordance with the reaction (6a) (see also eqn. (6), p. 455):

$$NH_4NO_3 \longrightarrow NH_3 + HNO_3\,(gas) - 521\ kcal/kg \qquad (6a)$$

This is an endothermic reaction of non-explosive character. It is evident from reaction (6a) why ammonium nitrate becomes acid during storage. Owing to the presence of free nitric acid in ammonium nitrate, its admixture with nitroglycerine may cause the latter to decompose in the course of time. Hence a little calcium carbonate, e.g. 0.3%, is very often added to ammonium nitrate destined for the manufacture of explosives including nitroglycerine.

At any temperature below the melting point, that is below 160°C, no chemical reactions occur except (6a) as mentioned already.

Pure ammonium nitrate when hermetically confined can be made to explode by rapid heating to a temperature above 200°C. Thus, for example Herguet [34] reports that ammonium nitrate confined hermetically undergoes an explosive decomposition on being heated to a temperature of 260–280°C. On the other hand attempts to bring about an explosion of ammonium nitrate that was not perfectly confined failed. Sherrick [35] has established that ammonium nitrate non-hermetically confined does not decompose explosively due to a thermal reaction, but will do so if brought in contact with molten iron.

The ease of detonation of ammonium nitrate is greatly influenced by its density. This was studied in detail by Fukuyama [36]. He prepared porous ammonium nitrate. The porous state appears at the transition points of 125 and 84°C when cooled. After the transition, the salt reserves its normal, less porous state. By rapid cooling the porous state can be preserved.

Table 112 gives the sensitiveness to initiation of low density and ordinary ammonium nitrate according to Fukuyama. Samples were loaded in a steel pipe of 12.5/16.5 mm dia. 50 mm length.

TABLE 112*

	Ammonium nitrate								
	of low-density						ordinary		
Loading density, g/cm³	0.5	0.6	0.7	0.8	0.9	1.0	0.8	0.9	1.0
Weight of initiator (mercury fulminate–chlorate mixture)									
0.3 g	*I*	*I*	*N*						
0.4	*E*	*E*	*I*						
0.5			*E*	*N*	*N*	*N*			
0.75				*I*	*I*	*N*			
1.0				*E*	*E*	*E*	*N*	*N*	
1.4							*E*	*E*	*I*
No. 6 detonator and 2 g TNT									*I*
No. 6 detonator and 4 g TNT									*E*

* Abbreviations: *N* – no explosion, *I* – incomplete explosion, *E* – explosion or detonation.

The rate of detonation of low-density ammonium nitrate was also determined by Fukuyama [36] (Table 113) at different temperatures in steel pipes of 35/40.4 mm dia. The initiation was by a No. 6 detonator.

In steel tubes of smaller diameter at room temperature, at the loading density 0.5 g/cm³, the rates of detonation were:

in 12.5/16.5 mm dia.	1520–1550 m/sec
in 27/32 mm dia.	1690–1740 m/sec

Fukuyama also studied the sensitiveness and the rate of detonation of ammonium nitrate containing water.

He found that ammonium nitrate containing 5–8% of water at a loading density 0.5 can be brought to detonation by a very strong initiator such as a No. 6 detonator with 15 g of TNT. With a 60 g TNT detonator, ammonium nitrate of even 10% water content can detonate in a 35/40.4 mm steel tube at a rate of 1900 m/sec.

TABLE 113*

Temperature °C	Loading density g/cm³	Rate of detonation m/sec	Loading density g/cm³	Rate of detonation m/sec
20	0.67	1760	1.0	*N*
50	0.67	1900	1.0	*N*
70	0.60	1900	1.0	*N*
90	0.60	1900	0.93	*I*
100	0.65	2170	0.93	*I*
110	0.65	2170	0.90	*I*
120	0.60	2000	0.84	1250
130	—	—	0.79	1530
140	0.65	2170	0.74	1570

* Abbreviations: *N* — no explosion, *I* — incomplete explosion.

The sensitiveness of ammonium nitrate to impact is relatively low: explosion takes place when a 10 kg weight is dropped from a height of 20 cm. The sensitiveness to shock increases with increasing of temperature, as shown in Table 114, published by Rinkenbach [42]:

TABLE 114

THE EFFECT OF THE TEMPERATURE ON THE SENSITIVENESS TO SHOCK OF AMMONIUM NITRATE

Temperature, °C	25	75	100	150	175 fused
height of fall a 2-kg weight, cm	79	71	69	69	50

The sensitiveness of fused ammonium nitrate is distinctly higher, and approximates to that of TNT. Ammonium nitrate does not take fire from the hot flame produced by a safety fuse.

The rate of detonation of ammonium nitrate depends to a large extent on the degree of fineness, the initiator, the density, and the confinement of the charge. It varies within wide limits, from 1100 to 2700 m/sec.

The net expansion in the lead block, as reported by different authors, varies between 180 and 220 cm³.

Many years' experience indicates that pure ammonium nitrate containing no organic substances detonates with greater difficulty than one containing organic substances. The well known explosion on the ship "Texas City" in April, 1947, was originated by the inflammation of an ammonium nitrate made in U.S.A. that contained 1% of mineral oil and 5% of kaolin. In order to prevent the propagation of fire both the ventilation channels and the doors in the partitions separating the

store rooms were shut. This resulted in an increase of pressure within the storage holds which ended by an explosion.

This accident caused a re-investigation of the explosive properties of ammonium nitrate mixed with fuel oil. A considerable amount of work was done by several authors particularly in the Explosives Research Laboratories, U.S. Bureau of Mines.

Cook and Talbot [37] found that the highest sensitiveness of ammonium nitrate to initiation by detonation exists when ammonium nitrate contains 0.75–1.5% of paraffin oil. It can be detonated by a No. 6 detonator.

Brinkley and Gordon [38] have shown that some compositions can be brought to detonation with considerable ease, and the maximum sensitiveness is at *ca.* 2–4% of oil content.

This was confirmed by Van Dolah [39]. The latter also determined the rate of detonation of paper cartridges of prilled ammonium nitrate with 4% fuel oil at a density of 0.95:

in 1.25 in. dia.	2980 m/sec (No. 8 detonator)
in 1.87 in. dia.	3750–3760 m/sec (No. 6 and 8 detonators)

Also according to Van Dolah ammonium nitrate–oil mixtures offer a certain dust explosion hazard and any electric equipment (switches controls, motors, lights) located in the plant should conform to the safety requirements or should be installed outside the plant. In order not to increase the dust explosion hazard no liquid hydrocarbon fuel with higher volatility than No. 2 Diesel fuel (minimum flash point of 145°F, ASTM closed-cup procedure) should be used as an admixture to ammonium nitrate. More volatile fuels, such as gasoline, kerosine or No. 1 Diesel fuel cannot be recommended according to Van Dolah, as they would seriously increase the hazard of a vapour explosion.

It has been suggested by Lee and Akre [40] that fertilizer grade ammonium nitrate containing "inert-coating" and fuel oil can be used as a blasting explosive. Indeed it became a useful explosive in open pit blasting. This is described in detail in Vol. III.

Tournay, Murphy, Damon and Van Dolah [41] examined the fumes produced by the detonation of ammonium nitrate–fuel mixtures. They came to the conclusion that carbon monoxide formation is within the allowed limits. However, the concentration of nitric oxide and nitrogen dioxide is much higher than in typical dynamite compositions. On the ground of these experiments they expressed the view that ammonium nitrate–fuel compositions should not be recommended for underground blasting.

An unconfirmed hypothesis was also formulated that ammonium nitrate in the presence of sulphuric acid undergoes dehydration to the formation of nitramine (Vol. III) which is a strong and unstable explosive compound.

A double salt of ammonium nitrate and sulphate, defined by the formula $2NH_4NO_3 \cdot (NH_4)_2SO_4$, is capable of detonating with a rate of 1000–1400 m/sec

provided an exceptionally strong initiator and completely hermetic confinement are used (Kast [33, 43]). However, the detonation train of this double salt has a tendency to break up after travelling a short distance (see also Blinov [43a]).

It has been suggested (Cornet and Boodberg [44]) that the explosive properties of ammonium nitrate might be utilized for improving the ignition of the fuel in Diesel motors. For this purpose concentrated ammonium nitrate solution was added to the fuel containing 0.25% of emulsifier, thus producing an emulsion of aqueous ammonium nitrate in the fuel. Adding 4% of ammonium nitrate solution of 20% concentration, to a self-igniting fuel that ignites at 215°C reduced the self-ignition temperature to 207°C. The same amount of water without ammonium nitrate added to the fuel increased the self-ignition temperature to 220°C.

COMMERCIAL PRODUCT

Ammonium nitrate for explosive manufacture should conform with the following purity requirements in accordance with the Soviet standard (GOST 2–40):

colour	white or yellowish
ammonium nitrate content	99.5%
maximum moisture percentage	0.5% type A (fine crystals) 0.8% type B (larger crystals)
reaction	neutral
non-volatile mineral content	max. 0.15%
water-insoluble material	max. 0.08%
salts of sulphuric acid calculated as $NH_4(SO_4)_2$	max. 0.15%
organic substances (oxidizable)	traces

According to the U.S. Standards ammonium nitrate for production of military explosives should contain: 99.0% of NH_4NO_3, no more than 0.02% free nitric acid, 0.18% of water-insoluble material, 0.50% of ammonium sulphate and 0.5% of ammonium chloride. The product should be free from alkalis and metal nitrates. A substance of similar purity is used for the manufacture of mining explosives.

In the U.S.A. ammonium nitrate is available commercially in different forms. There are prilled, flaked and granular forms.

Various brands of ammonium nitrate uncoated or coated with clay or kieselguhr, and with other inorganic or organic substances, such as fuel oil are produced.

Methods of manufacture ammonium nitrate are described in specialist books on inorganic technology and technology of nitric acid and ammonium salts. However, the method of manufacture of low density prilled ammonium nitrate merits special attention as it can be used to manufacture low density coal mine explosives.

Prilled ammonium nitrate is prepared essentially by methods involving the following steps:

The ammonium nitrate solution (from the neutralizer) is evaporated to *ca.* 96% concentration in the steam heated vacuum evaporator. The concentrated solution is sprayed into the top of the prilling tower, where it falls through an upward flow of air supplied by blowers at the base of the tower. During its fall it is cooled and solidifies to round pellets or "prills" of the desired size.

The prills are drawn off continuously from the hopper bottom of the tower by means of a conveyer and fed to the pre-drier, then to the drier and cooler. From the cooler the prills are elevated to a double deck screen. Oversize and undersize are dissolved in water and returned to the neutralizer or used for producing "nitrogen solutions".

The intermediate size is dusted with a small amount of coating material (diatomaceous earth or kaolin) in a rotary coating drum.

Fertilizer grade ammonium nitrate prilled with fuel oil is generally used in the U.S.A. for making explosives other than permitted types (see Vol. III).

Ammonium nitrate prepared from ammonia obtained by the dry distillation of coal should not be used as component of any explosive material because of the ammonium thiocyanate and pyridine present in it (the latter as nitrate). When the ammonia liquor from dry distillation of coal was the sole source af ammonia and ammonium nitrate, decomposition of mixtures containing ammonium nitrate with TNT (amatols), was brought about: at the melting point TNT reacted with ammonium thiocyanate or with pyridine nitrate and evolved gaseous products. Minute traces of these impurities were sufficient to cause abundant gas evolution to develop during the fusion, pouring, and cooling of amatol.

HYDRAZINE NITRATE

Hydrazine nitrate, $\overset{\ominus}{NH_2}\cdot\overset{\oplus}{NH_3}\cdot\overset{\ominus}{NO_3}$, exists in two crystalline forms of different melting temparatures: the stable form melts at 70.7°C, while the labile melts at 62.1°C. In contact with water hydrazine nitrate dissolves with great ease to form a strongly acid solution. In the fused state it reacts rapidly with several metals, such as zinc and copper. Hodgkinson [45] explains this behaviour as due to the formation of azides under these conditions. In the presence of nitrites, hydrazine nitrate forms salts of hydrazoic acid.

According to Kast [46] hydrazine nitrate is practically stable at 75°C, since after 9 months of heating it lost barely 0.7% of the weight. It does not explode on heating to 360°C. The substance is sensitive to friction and to impact, resembling tetryl, and according to Médard [47] resembling cyclonite. Compressed under a pressure of 3000 kg/cm^2 it has the density 1.64 g/cm^3.

Médard [47] established that hydrazine nitrate is an explosive that is readily detonated by an initiating cap, even when the density achieved by loading the product in the molten state is high (1.62 g/cm^3). The rate of detonation of a cartridge, 30 mm dia., placed in a cardboard paper case is:

density, g/cm³	rate, m/sec
1.00	3900
1.20	5200
1.25	5640
1.30	5440
1.45	5000
1.57	3250

The expansion in the lead block is 20% larger than with picric acid. According to Kast [46] it is 320 cm³. Hydrazine nitrate is slightly less hygroscopic than ammonium nitrate. It is stable at temperatures within the range 110–120°C. Since its melting point is low hydrazine nitrate is valuable for preparing fusible mixtures with ammonium nitrate. An admixture of about 10% of hydrazine to ammonium nitrate significantly decreases the difficulty of provoking detonation of the latter compound.

Hydrazine dinitrate is an unstable substance, hence it is of no practical value.

FLUORINE NITRATE

Moissan [48] observed that explosions took place when fluorine was introduced into concentrated nitric acid. Afterwards it was found that more dilute nitric acid, e.g. 4*N* HNO_3, reacts with fluorine to form an explosive product. The reaction product was isolated by Cady [49] who has also determined that both the chemical composition and the molecular weight of the product are well in line with the formula NO_3—F.

Fluorine nitrate, under normal conditions, is a colourless gas with an irritant smell that is condensed at a temperature of about —42°C. It combines with potassium iodide and with potassium hydroxide as shown in the equations:

$$NO_3F + 3I^{\ominus} \longrightarrow I_3^{\ominus} + F^{\ominus} + NO_3^{\ominus} \tag{9}$$

$$NO_3F + 2OH^{\ominus} \longrightarrow \tfrac{1}{2}O_2 + F^{\ominus} + NO_3^{\ominus} + H_2O \tag{10}$$

According to Yost and Beerbower [50] fluorine nitrate explodes when heated within the temperature limits of 200 and 300°C. Sometimes the liquid or solid substance explodes without any obvious cause.

METHYLAMINE NITRATE

Naoúm [51] proposed the use of methylamine nitrate as an ingredient of fusible explosives. During World War II it was employed in Germany, under the name Man-Salz as one of components of a fusible explosive blend used for filling missiles, along with sodium nitrate and cyclonite.

Methylamine nitrate was obtained by treating methylamine with concentrated nitric acid (66%). The explosive strength of methylamine nitrate exceeds that of TNT. Its hygroscopicity, which is even higher than that of ammonium nitrate, is a disadvantage.

On experimental grounds Le Roux [52] reports that the tendency of methylamine nitrate to detonation is not high. At a density of 0.9 g/cm³ it is completely decomposed by a 2-g detonating cap along a short space only. A much stronger detonator, con-

taining up to 40 g of PETN, is necessary to cause the detonation to propagate on a larger area. Likewise the substance is scarcely sensitive to shock.

The heat of explosion of methylamine nitrate is 1200 kcal/kg, the volume of gases produced being $V_0 = 834$ l./kg. When initiated by 40 g pentaerythritol tetranitrate (PETN) it detonates in steel pipes of 30/33 mm diameter, with the following rates:

density, g/cm³	rate of detonation, m/sec
0.90	3140
1.10	3280
1.20	2860
1.30	does not detonate

It produces a net expansions of 325 cm³ in the lead block.

Methylamine nitrate is a stable compound. Marked thermal decomposition starts at 195°C, and on raising the temperature to 235°C, oxides of nitrogen are developed. A sample of the substance thrown into a test-tube heated to 375–390°C explodes in 7 sec.

Le Roux found that methylamine nitrate forms the following eutectics:

methylamine nitrate	67%	m.p. 55.5°C
ammonium nitrate	33%	
methylamine nitrate	92%	m.p. 84°C
sodium nitrate	8%	

TETRAMETHYLAMMONIUM NITRATE, $(CH_3)_4\overset{\oplus}{N}\overset{\ominus}{N}O_3$

According to le Roux [53] tetramethylammonium nitrate has no explosive properties: it did not detonate even when initiated by a strong charge of PETN. Attempts to provoke explosive decomposition by impact failed. Le Roux suggested that the compound might be used as an ingredient of explosive mixtures, for instance blended with cyclonite or incorporated in a fusible mixture with ammonium nitrate (see Vol. III).

Tetramethylammonium nitrate has the form of white crystals, soluble in water, m.p. 410°C. Its density is 1.25 g/cm³. Compressed under 3400 kg/cm² it has a density of 1.22 g/cm³.

GUANIDINE NITRATE

$$\begin{array}{ll} \overset{\oplus}{NH_3}\overset{\ominus}{NO_3} & NH_2 \\ | & | \\ C{=}NH & C{=}\overset{\oplus}{NH_2}\overset{\ominus}{NO_3} \\ | & | \\ NH_2 & NH_2 \end{array}$$

Guanidine nitrate exists as crystals melting at 215–216°C, soluble in water (4.64 g in 100 ml of water) and in alcohol. It may be recrystallized from the either of these solvents.

PROPERTIES

Guanidine nitrate has found application as a component of fusible explosive mixtures containing ammonium nitrate (see Vol. III). Further, it represents the most important intermediate product for the commercial manufacture of both nitroguanidine and aminoguanidine. Gaensa [54] proposed the use of guanidine nitrate as an ingredient of propellants, while Gérard [55] suggested using it as a component of fusible mixtures containing ammonium nitrate.

T. Urbański and Skrzynecki [57] investigated the ammonium nitrate–guanidine nitrate system, and established that the substances form an ordinary eutectic containing 26 parts of guanidine nitrate melting at 127.7°C. The formation of the eutectic composed of guanidine nitrate and nitroguanidine, and of the ternary eutectic with ammonium nitrate and nitroguanidine, will be discussed in Vol. III. The most important chemical property of guanidine nitrate is its ability to be converted into nitroguanidine in the presence of dehydrating agents, for instance sulphuric acid (Vol. III).

Guanidine nitrate, being a rather weak explosive, can be detonated only with difficulty.

Patart [58] determined experimentally that the "force" f of guanidine nitrate is 5834 m and hence he calculated the temperature of explosion $t = 930$°C. This low explosion temperature is probably a consequence of incomplete detonation due to the compound's poor aptitude to detonation.

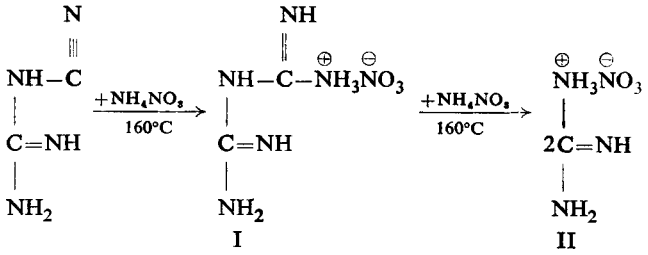
T. Urbański, Kapuściński and Wojciechowski [59] reported that guanidine nitrate produced a net expansion in the lead block amounting to only 140 cm^3 (Kast [46] reported 110 cm^3). The rate of detonation was not determined, since the substance could only undergo a partial detonation. Even the addition of 4% of TNT did not bring about a total detonation. According to Médard [59a] guanidine nitrate can be brought to detonation at a density 1.0 in a steel tube 36/42 mm by using 50 g of NP. Mn 95/5 (a mixture of 95% PETN and 5% nitronaphthalene) as a primer. He found the rate to be 3700 m/sec.

MANUFACTURE

A. W. Hofmann [56] was the first to prepare guanidine nitrate from guanidine hydrochloride which he obtained by treating chloropicrin with an alcoholic solution of ammonia at 100°C. In 1908 the method of manufacturing guanidine salts by way of fusing or heating dicyandiamide with ammonium salts was worked out by Stickstoffwerke at Spandau, Germany. On the development of the synthetic ammonia industry, the raw materials for making guanidine nitrate became readily available.

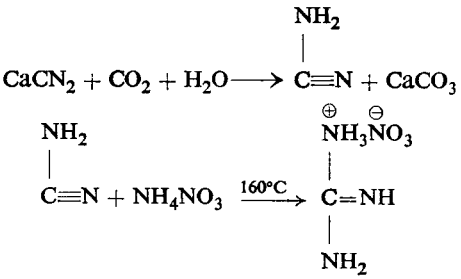
The most widely used method for manufacturing guanidine nitrate was described in detail by Davis [60]. Its basic principle is heating dicyandiamide with two equivalents of ammonium nitrate at 160°C. Originally the mixture was fused

to form biguanide nitrate (guanylguanidine nitrate, (I)). On being heated in the presence of another mole of ammonium nitrate this salt is gradually converted into guanidine nitrate (II):



Biguanide is a strong base, hence it brings about the decomposition of ammonium nitrate, accompanied by evolution of free ammonia. In order to avoid the loss of ammonium nitrate, the latter should be used in excess. For a long time this method was the most widely used for the production of guanidine nitrate, and nitroguanidine. Another process used for manufacturing nitroguanidine from dicyandiamide is described in Vol. III.

A slightly different method of guanidine nitrate manufacture was introduced in German plants during World War II. It consists in the chemical combination of ammonium nitrate and cyanamide as defined by eqns. (12) and (13).



(12)

(13)

Both reactions are carried out in the same reactor. A diagrammatic outline of the plant for guanidine nitrate manufacture is illustrated by Fig. 173 [61].

An autoclave (*1*) is supplied with an aqueous solution that contains 600 g of ammonium nitrate and 40 g of ammonia per litre. Calcium cyanamide in the ratio of 500 g $CaCN_2$ to every litre of solution is then added from container (*2*) after being weighed at (*3*). The autoclave is closed, carbon dioxide is introduced, while the contents are cooled with water so that the temperature does not exceed 100°C. When no more carbon dioxide is absorbed, the supply is stopped, and so is the inflow of cooling water. The reaction mixture is now steam heated to 160°C. Afterwards a communicating valve joining the autoclave (*1*) with a second autoclave (*15*) is opened. The other vessel (*15*) is filled with ammonium nitrate solution prepared for the next charge. In this way the major part of the ammonia passes from autoclave (*1*) over to autoclave (*15*). After the reaction is finished the mixture is raised from the auto-

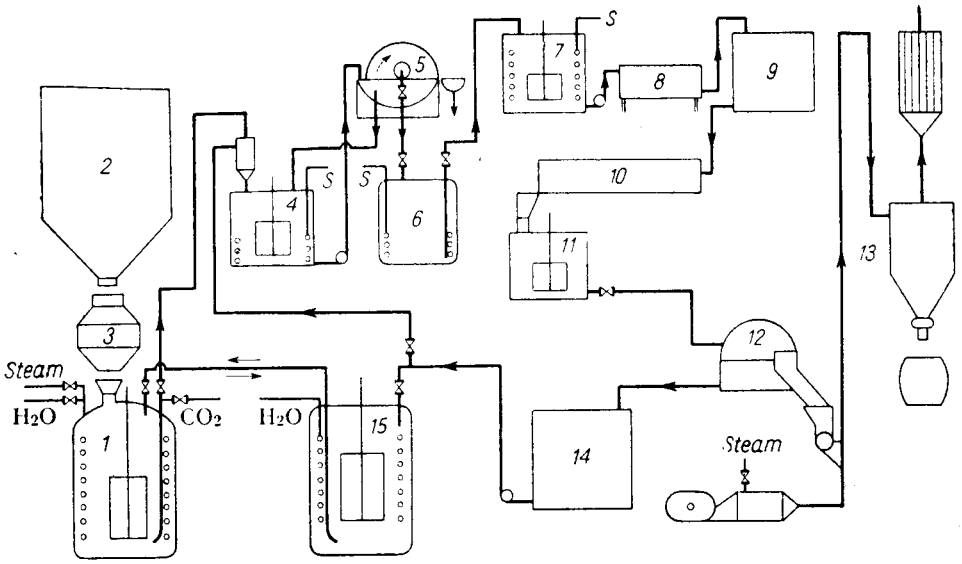
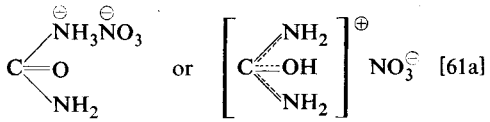


FIG. 173. Flow-sheet of the manufacture of guanidine nitrate [61].

clave to the tank (*4*) and then to a rotating filter (*5*). In the tank (*4*) calcium carbonate suspended in guanidine nitrate solution is diluted with the mother liquor from a tank (*14*) in the ratio 1:1, and the calcium carbonate is separated on the filter (*5*), and rinsed with water. The guanidine nitrate solution, together with the washings from rinsing the precipitate, is passed over the receiver (*6*) to the evaporator (*7*), where the whole solution is evaporated to a concentration of 300 g guanidine nitrate per litre. This solution is filtered hot in a filter press (*8*). The hot liquor collected in the tank (*9*) flows down to a crystallizer (*10*). In the crystallizer the solution is held until it cools to 20–25°C. Thereafter the crystallized guanidine nitrate together with its mother liquor is passed to the centrifuge (*12*), where the separation of crystals takes place. The product is then transported to the drier (*13*), and the mother liquor goes to the tank (*14*) from which it is pumped over to the autoclave. There sufficient ammonium nitrate is added to adjust its concentration to the initial 600 g/l. Then ammonia evolved in the preceding operation in the autoclave (*1*) is introduced so as to saturate the solution with 40 g NH_3 per litre. The yield of guanidine nitrate is 50–55% of theoretical.

UREA NITRATE



[61a]

m.p. 163°C

Urea nitrate is prepared by treating urea with dilute nitric acid, e.g. 34%. Choisy [62] proposed using it as an explosive. However, the manufacture of cheap urea

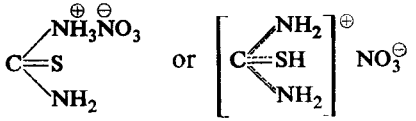
nitrate was only possible after the Bazarov–Fichter reaction (i.e. the synthesis of urea from carbon dioxide and ammonia) was developed on an industrial scale. Under action of dehydrating agents (e.g. sulphuric acid) it yields nitro urea (Vol. III).

Urea nitrate has not found practical application, since it is not stable enough, although according to Kast [46] the loss of weight after 14 days at 75°C was only 0.2%. Decomposition into carbon dioxide, nitrous oxide, ammonium nitrate and urea takes place even at 140°C, and at 180°C decomposition is rather violent. Nevertheless a small sample of the substance does not explode.

Urea nitrate is insensitive to friction and to impact. The density of the substance subjected to a pressure of 1500 kg/cm^3 is 1.59 g/cm^3. In the lead block test it caused an expansion of 260 (Kast) or 270 cm^3 (T. Urbański, Kapuściński, Wojciechowski [59]). It detonates somewhat better than ammonium nitrate and guanidine nitrate, but a No. 8 detonator did not provoke complete detonation. Médard [59a] reported that urea nitrate gives a relative figure of the lead block expansion 79.6 (picric acid = 100) and the rate of detonation of 30 mm dia. charges is:

density 0.85 (in paper tube) 3400 m/sec
density 1.20 (in steel tube) 4700 m/sec.

THIOUREA NITRATE



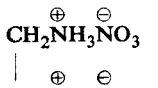
m. p. 130–134°C

Thiourea nitrate was prepared by Palamo Coll [62a] by the action of dilute nitric acid ($d = 1.33$) on thiourea at 5–10°C. The same author prepared nitrothiourea by the action of thiourea nitrate with acetic anhydride (Vol. III).

Its decomposition temperature on a hot copper plate (induction period $\tau = ca.$ 0.5 sec) is 410°C, as determined by T. Urbański and Kurcewicz [62b].

The same authors found that thiourea nitrate is a weak explosive giving a lead block expansion of 150 cm^3.

ETHYLENEDIAMINE DINITRATE



m.p. 185–187°C

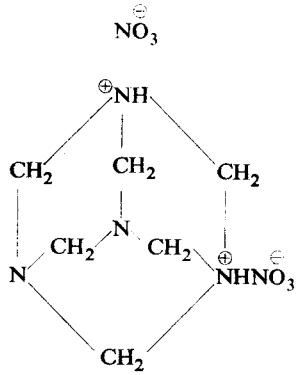
This substance was suggested as a component of explosive materials by Stähler [63]. It was introduced in Germany during World War II, where it was used as an

ingredient of fusible mixtures containing ammonium nitrate (see Vol. III) under the name PH-Salz. The drawback of ethylenediamine dinitrate lies in its hygroscopicity.

Le Roux [64] reports that ethylenediamine dinitrate forms an eutectic with ammonium nitrate 50/50, the fusion temperature of which is above 100°C. He suggested using a mixture composed of 50% of ammonium nitrate and 50% of ethylenediamine dinitrate instead of amatol 50/50.

Ethylenediamine dinitrate is a chemically stable compound. After being kept for 14 days at 75°C it lost only 0.38% of its original weight. It does not explode on heating up to 350°C. Its explosive strength is greater than that of TNT or picric acid, but slightly lower than tetryl. The density of ethylenediamine dinitrate pelleted under a pressure of 1500 kg/cm^2 was 1.49 g/cm^3 according to Kast [46]. Its expansion in the lead block amounts to 345 cm^3. The rate of detonation can reach 6800 m/sec (30 mm dia. cardboard tube) according to Le Roux.

HEXAMETHYLENETETRAMINE DINITRATE



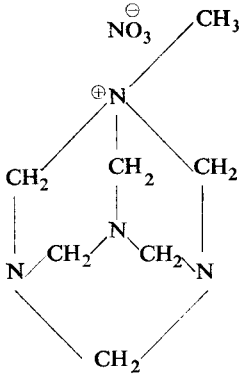
I (m.p. 160°C)

Hexamethylenetetramine dinitrate ("hexamine" dinitrate) itself is of no importance as an explosive. However, it plays a considerable part in the production of cyclonite by one of the methods described in Vol. III. Hexamine dinitrate is prepared from hexamine by treating it with 50–70% nitric acid, at a temperature not above —15°C.

Foss, Hirst, Jones, Springall, A. T. Thomas and T. Urbański [65] have established that boiling an aqueous solution of hexamine dinitrate causes the substance to transform into methylhexamethylene mononitrate (II).

The base of the nitrate (II) has proved to be identical with Knudsen's base for which an incorrect formula was given by Knudsen [66], and identical with the product (II) of interaction of methyl nitrate with hexamine described by Hahn and Walter [67].

Observations also made by Foss *et al.* [65] showed that a certain amount of the nitrate (II) is produced during prolonged storage of hexamine dinitrate owing to partial decomposition followed by the reduction of formaldehyde to a methyl radical.



II (m.p. 192°C)

This is of practical importance, for the presence of the substance (II) in (I) may reduce the purity of cyclonite.

NITRATES OF ETHANOLAMINE NITRIC ESTERS

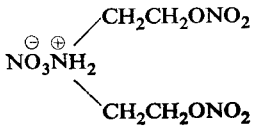
Naoúm [68] has drawn attention to the nitric acid salts of ethanolamine nitric esters (O-nitrated ethanolamines), i.e. mono-, di- and triethanolamine nitrate salts, as substances suitable for explosives. Nitration of a mixture of all three ethanolamines furnishes an oil-like, insufficiently stable product, readily decomposed with the evolution of oxides of nitrogen. The individual substances are crystal products soluble in water, in which they are hydrolysed.

Ethanolamine nitric ester nitrate (ethanolamine dinitrate) $NO_3NH_3CH_2CH_2ONO_2$ is a solid melting at 103°C. According to Naoúm this compound can be prepared by nitrating ethanolamine [68]. Aubry [69] has reported that a yield of 90–96% can be achieved in this reaction. This method of preparation has not been confirmed by some authors. Serious disadvantages of the substance include its inclination to absorb moisture, and the readiness with which it loses nitric acid owing to the weakly basic properties of the amine [70].

The nitric acid produced causes decomposition, hence the product has a low chemical stability.

Ethanolamine dinitrate is a strong explosive, since its expansion in the lead block test, as determined by Naoúm, is 430 cm^3. It has a remarkably low sensitiveness to impact. Nevertheless its tendency to dissociate and to form free nitric acid and its low stability prevent any practical application.

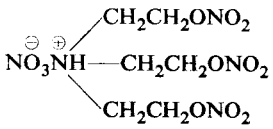
Diethanolamine dinitric ester nitrate (diethanolamine trinitrate)



This compound has the same drawbacks and advantages as that described above. Médard [71] has published the relevent physical data. The melting point of diethanolamine trinitrate is 123.8°C (previously values of 116 and 120.5°C were published). The pure substance is non-hygroscopic. Its sensitiveness to shock is insignificant: a 10-kg weight dropped from the height of 1.0 m caused 34% explosions. The rate of detonation at a density of 1.0 g/cm^3 amounts to 5560 m/sec, whilst at a density of 1.40 g/cm^3 it is 6510 m/sec. The lead block test figure is some 30% higher than that of picric acid. The most serious disadvantage of this explosive is that its stability is not high enough: a specimen kept at 130°C deflagrates after 8 min whilst at 85°C an explosive decomposition takes place within 5 hr.

However, it is not unimportant as it is an intermediate product in the manufacture of diethanolnitramine dinitrate (DINA, see Vol. III).

Triethanolamine trinitric ester nitrate (triethanolamine tetranitrate)



(m.p. 62°C)

Its properties resemble those of the preceding substance. One molecule of nitric acid is readily lost by the compound, which is then transformed into triethanolamine trinitrate. The latter is also unstable and inclined to undergo decomposition. Diphosphoric salt of the trinitric ester was claimed to be an effective remedy against *angina pectoris*, instead of nitroglycerine.

OXONIUM NITRATES

Oxonium nitrates have been known since 1835 [72]. They were originally described as addition compounds of aldehydes and ketones with nitric acid [72, 73]. Reddelien [74], who carried out particularly extensive studies, represented the structure of the compounds diagrammatically as $\diagdown C = O \cdots HONO_2$. Recently, Hofman, Stefaniak and T. Urbański [75] produced evidence of the oxonium structure of the additive compounds, on the basis of infra-red absorption spectra:

The products of addition of nitric acid to ethers also possess the same oxonium structure:

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CHAPTER XX

SALTS OF OXY-ACIDS OF CHLORINE

SALTS OF CHLORIC ACID

PURE sodium and potassium chlorates do not possess explosive properties, but in earlier times were important components of the most widely used explosive mixtures (Vol. III). Also some complex salts of chloric acid possess initiating properties (Vol. III). Chlorates of nitrogen bases are explosives and deserve some attention. In particular, ammonium chlorate should be mentioned owing to the part it has played in the history of explosives.

AMMONIUM CHLORATE

Ammonium chlorate, NH_4ClO_3, is a substance that undergoes explosive decomposition according to the equation:

$$2NH_4ClO_3 \longrightarrow N_2 + 3H_2O + 2HCl + \tfrac{3}{2}O_2 + 459 \text{ kcal/kg} \qquad (1)$$

The rate of detonation of ammonium chlorate of density 0.9 g/cm^3 is 3300 m/sec, and its expansion in the lead block test is about 250 cm^3. Ammonium chlorate is sensitive to impact: it explodes if a 2-kg weight is dropped on it from a height of 15–20 cm. It takes fire from the flame produced by a safety fuse, and if confined the flame causes it to explode.

Ammonium chlorate is non-hygroscopic, but dissolves readily in water. It decomposes with ease on keeping at room temperature, and very promptly at slightly higher temperatures. Galhaar [1] has stated that in 7 weeks it lost 80% of its weight. Explosion occured at 40°C after 11 hr, and at 70°C after only 45 min.

Due to its low stability, the use of ammonium chlorate in explosive mixtures is out of the question. Furthermore it is not permissible to mix ammonium salts together with salts of chloric acid (e.g. ammonium nitrate with potassium chlorate, see Vol. III) [2].

HYDRAZINE CHLORATE, $\overset{\oplus}{N}H_2NH_3\overset{\ominus}{Cl}O_3$

Salvadori [3] studied the properties of hydrazine chlorate and established that it melts at 80°C, simultaneously exploding violently.

ETHYLENEDIAMINE CHLORATE

$$CH_2\overset{\oplus}{N}H_3\overset{\ominus}{Cl}O_3$$

$$CH_2NH_2$$

Suggestion that ethylenediamine chlorate might be used in explosive manufacture was made by Stähler [4] who reported the substance to be a very strong explosive, sensitive to impact. So far it has not found commercial application.

CHLORINE DIOXIDE

Having considered the explosive chlorates, the explosive properties of chlorine dioxide, ClO_2 should also be mentioned. Chlorine dioxide is a mixed chlorous–chloric anhydride

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3 \qquad (2)$$

There are several methods of manufacturing is on a commercial scale, for instance the calcination of oxalic acid blended with potassium chloride, treatment of sodium chlorite with chlorine, or of sodium chlorate with sulphur dioxide in the presence of concentrated sulphuric acid. Chlorine dioxide is utilized as a strong bleaching agent for cellulose, paper, flour, oils and such like, as well as a solvent for removing lignin from wood pulp.

Under normal condition it exists as a gas that it condensed at $+10°C$, and freezes at $-76°C$. In the condensed or solid state, chlorine dioxide explodes even while being poured from one vessel into another. The expansion produced in the lead block is 200 cm^3. It was recently suggested as a component in liquid propellants for rockets.

SALTS OF PERCHLORIC ACID

The explosive salts of perchloric acid are considerably more interesting than the explosive chlorates, since these are more stable and safer to handle. A few of them, for instance ammonium perchlorate, rank as components of explosive mixtures and rocket propellants. Some salts of perchloric acid possess initiating properties (Vol. III).

Others, for instance guanidine perchlorate, pyridine perchlorate, are among the strongest explosives.

Potassium perchlorate, a non-explosive compound, is an important ingredient in many mixed explosives. An excellent monograph on perchlorates was written by Schumacher [54].

AMMONIUM PERCHLORATE

There exist two crystalline modifications of ammonium perchlorate, NH_4ClO_4: an orthorhombic form below 240°C, and a cubic form above this point. An addition of small amount of some dyestuffs inhibits change of the crystalline forms [52].

The explosive properties of ammonium perchlorate are more marked than those of ammonium nitrate.

Ammonium perchlorate is used as a component of perchlorate high explosives. Lately it has been brought into prominence as a constituent of solid rocket fuels, the combustible components of which include such polymers as thiokol and methyl polymethacrylate (Vol. III). Hence a considerable interest has recently been taken in ammonium perchlorate.

Thermal decomposition

A study of the kinetics of the decomposition of ammonium perchlorate has been made by Bircumshaw and Newman [5]. The gaseous products, up to a temperature of 300°C, were found to be oxygen, chlorine, chlorine dioxide, nitrous oxide, nitrogen tetroxide, chlorine dioxide, hydrochloric acid, perchloric acid and water. The total volume of oxygen and nitrogen produced by unit weight of the solid showed practically no variation up to about 300°C.

The course of the reaction in the range 200–300°C was followed gasometrically by two methods: (1) by heating the salt *in vacuo*, condensing out all the gaseous products other than oxygen and nitrogen, and measuring the rate of increase of pressure with time in a constant volume apparatus, (2) by measuring the "build up" of pressure during 30 or 60 sec at fixed intervals of time.

Experiments were made on single crystals heated for varying lengths of time. It was shown by photo-micrographs that decomposition started at points on the surface and then spread inward and over surface (Fig. 174). The cross-section

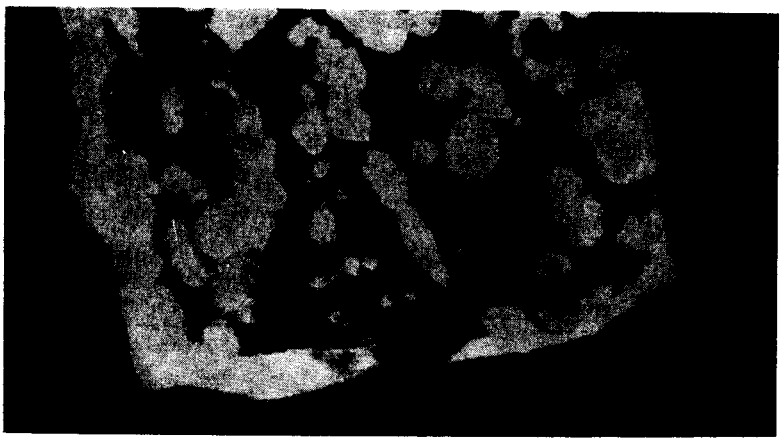


FIG. 174. Nuclei formed in crystals of ammonium perchlorate (Bircumshaw and Newman [5]).

of a crystal heated for a period to produce about half decomposition showed that the reaction spreads inwards, and demonstrated the presence of a definite interface between the decomposed and "undecomposed" material (Fig. 175).

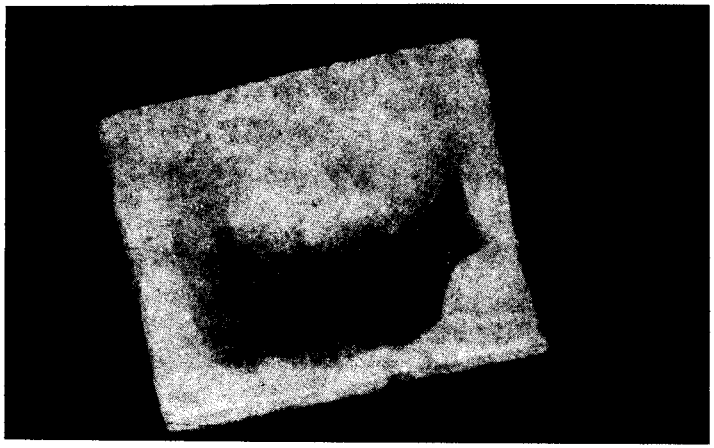


FIG. 175. Interface between the decomposed and undecomposed ammonium perchlorate (Bircumshaw and Newman [5]).

A most interesting and unexpected result was found in the lower temperature range (220–300°C). Only 30% by weight of the salt would decompose in spite of the fact that in plotting pressure as a function of time the usual sigmoid curve was obtained. The residue, which has a different physical appearance ("zeolytic") from the original crystalline salt, was found to be pure ammonium perchlorate with a trace of $H^{\oplus}$ and perhaps $NO_3^{\ominus}$ ions. It could be "rejuvenated" by exposure to a water vapour (after two days the salt again decomposed to the extent of 30% of its weight) and to the vapour of other liquids in which the salt was soluble. The extent of the rejuvenation depended on the solubility and the time of exposure. Experiments were made in which the original salt, both before and after a small amount of decomposition had occurred, was exposed to the gaseous products of decomposition. This was found to have no effect, so it was concluded that stoppage of decomposition was not due to poisoning of the reaction centres. The rejuvenation may be due to the same type of interface recrystallization.

The perchlorate was found to sublime *in vacuo* to some extent at all temperatures. A small pressure of inert gas was found to reduce the sublimation. The sublimate was found to be ammonium perchlorate with traces of $H^{\oplus}$ and $NO_3^{\ominus}$ ions. It decomposed with a reduced induction period at a slightly higher rate. It was found that sublimation continued after decomposition had stopped. It is curious that the vapour, which may or may not be dissociated, is not decomposed at these temperatures.

The variation in maximum rate (build up curves) with temperature is shown in Fig. 176. A rapid increase in the rate above 240°C might have been expected since the salt is then in the cubic form with both ions rotating, but evidently the cubic is the more stable form. The occurrence of the minimum could be due to the cubic form possessing the maximum stability at this temperature. Alternatively,

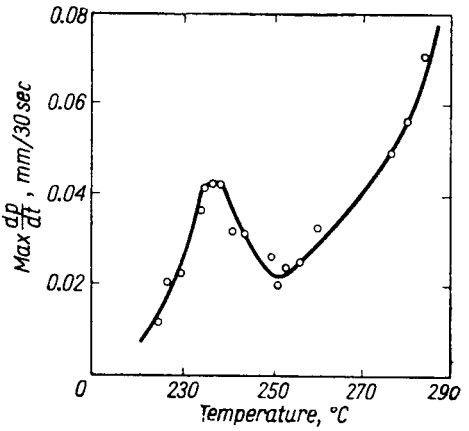


FIG. 176. Rate of decomposition of ammonium perchlorate. Variation with temperature according to Bircumshaw and Newman [5].

assuming that the cubic is more stable than the orthorhombic form, the fall in rate between 240 and 250°C might be due to the presence of a mixture of the two forms (allowing for transition time). The more thermally stable form is present in increasing quantity as the temperature approaches 250°C.

Experiments were made to determine the influence of the surface area on the rate of decomposition. Five fractions were obtained and the effect of the surface area was determined from the rate curves at a temperature of 230°C. By plotting the maximum rate as a function of the total surface area it was found the rate rose steeply to a maximum at a certain size as the particle size decreased, and then decreased again. Mampel [6] predicted that a decrease in the rate would occur at a particular particle size. The period of acceleration will come to an end just after the expanding reaction zones begin to interfere with one another, and this will happen sooner with small than large particles. On decreasing the size, the effect of increasing the area first comes into play, but after a certain size, the above effect begins to operate and the rate decreases again.

The recent experiments by Galwey and Jacobs [7a] were mainly dedicated to examining the thermal decomposition of ammonium perchlorate above *ca.* 350°C. They found the decomposition differs in several respects from that below this temperature, complete decomposition occurs, whereas at low temperatures a residue of ammonium perchlorate always remains as described above.

They suggest that the rate determining step for the high temperature thermal decomposition is a proton-transfer on the surface of the solid followed by oxidation of the ammonia gas by radicals resulting from the decomposition of perchloric acid. It seems probable that perchloric acid should undergo fast decomposition at these temperatures, generating oxygen atoms which oxidize the ammonia:

$$2HClO_4 \longrightarrow H_2O + Cl_2O_7$$

$$Cl_2O_7 \longrightarrow 2Cl_2 + 7O_2$$
$$4NH_3 + 5O_2 \longrightarrow 6H_2O + 4NO$$

The scheme accounts for the major products found by Dodé [8] who represented the overall reaction as follows:

$$2NH_4ClO_4 \longrightarrow 4H_2O + 2NO + O_2 + Cl_2$$

A few experiments made by Bircumshaw and Newman [5] at a temperature of 400°C in a spiral gauge apparatus agreed with the conclusion that the decomposition was quite different from that at the lower temperatures. There was no induction period, the whole of the reaction was a decelerating one, and decomposition went to completion. The reaction appeared to follow a simple power law, $p = kt^n$, where n varied with temperature and was always less than unity.

Although no solid products are produced in this decomposition, nevertheless the reaction type must be

$$\underset{\text{solid}}{A} \longrightarrow \underset{\text{solid}}{B} + \underset{\text{gas}}{C} + \underset{\text{gas}}{D}\ldots$$

the undecomposable residue functioning as the solid B and providing the interface at which the reaction takes place. The sigmoid curves obtained were explicable, in the accelerating phase in terms of the Prout–Tompkins [10] accelerating equation,

$$\log \frac{p}{p_f - p} = k_1 t + \text{constant}$$

where p is the pressure at time t, p_f the final pressure, i.e. the pressure at $\cong 30\%$ decomposition; on the basis of the power expression, $p = kt^n$, $n \cong 6.0$. In the decelerating phase, the Prout–Tompkins equation,

$$\log \frac{p}{p_f - p} = k_2 t + \text{constant}$$

and the unimolecular decay law both gave straight lines.

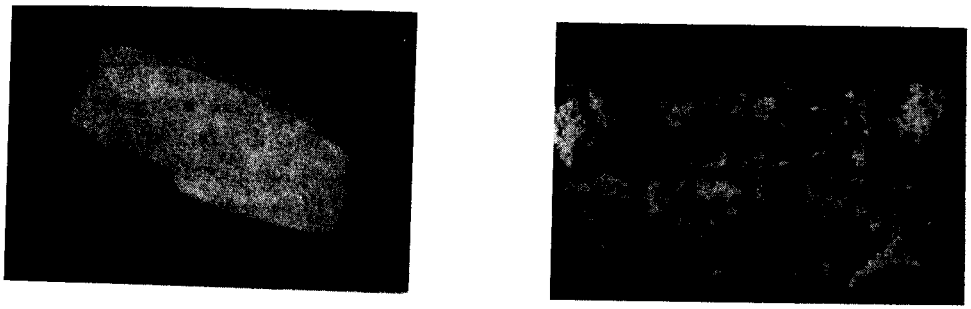
From the rate constants obtained, the activation energy was found to be 27.8 and 18.9 kcal/mole for the orthorhombic and cubic forms respectively.

According to Glasner and Makovky [13] the activation energy of decomposition of ammonium perchlorate is 31.0 kcal/mole in the temperature range 440–478°C.

Recently Freeman, Anderson and Campisi [11] examined the effects of X-rays on the chemical reactivity of ammonium perchlorate in the solid state. They found that pre-exposure of ammonium perchlorate to high energy radiation greatly affects the way it decomposes thermally.

In unirradiated ammonium perchlorate crystals decompose at preferential regions that occur along intermosaic boundries where crystal structure imperfections occur (Fig. 177a). The reaction sites in X-ray irradiated samples occur in a homogeneous-like manner throughout the crystal. Nuclei for reaction are distributed uniformly throughout the crystal (Fig. 177b).

An electron spin resonance study by Hyde and Freeman [12] revealed that ammonia radical ion $NH_3^{\oplus}$ form when ammonium perchlorate is exposed to X-rays. This radical ion was found to be stable in the ammonium perchlorate lattice up to 120°C. It is not formed during thermal decomposition and is not present in ammonium perchlorate sublimate.



a *b*

FIG. 177. Microphotographs of ammonium perchlorate in transmitted light: (a) unirradiated crystal, (b) X-ray irradiated crystal (Freeman, Anderson and Campisi [11]).

The activation energy of decomposition of both irradiated and unirradiated ammonium perchlorate in the orthorhombic form below 240°C is *ca.* 18.0 kcal/mole according to Freeman. This seems to indicate that irradiation of ammonium perchlorate does not change the decomposition mechanism but provides many more nucleation sites.

The authors have also found that chlorate ion is present after irradiation. The chlorate ion may provide intermediate species which act as catalysts.

The introduction of silver ions which act as electron traps enhances the radiation-induced changes in the thermal decomposition of ammonium perchlorate. Irradiated samples containing silver show thermal decomposition similar to samples without silver, but which received a considerably greater radiation dose.

The influence of a number of catalysts on the decomposition of NH_4ClO_4 has been investigated [9]. Salt crystallized out from solutions containing traces of free perchloric acid decomposed with a much shorter induction period. Ammonia had the reverse effect. Mixing the salt with a number of oxides was also tried. Calcium oxide slowed down the reaction. Aluminium oxide had no effect. Ferric oxide had a marked catalytic effect, but the greatest effect was observed with manganese dioxide. It gave complete decomposition at 230°C without sublimation, unlike the other cases. Galwey and Jacobs [7a] investigated the thermal decomposition of ammonium perchlorate with MnO_2 at 137–212°C. They found that the reaction proceeds in two stages: the first being the catalysed decomposition of NH_4ClO_4 (activation energy 32 kcal/mole) and the second the decomposition of NH_4ClO_4 which is not influenced by the presence of MnO_2. See also Makovky and Salmon [55].

The same authors [7b] examined the thermal decomposition of ammonium perchlorate with charcoal (see also Vol. III). At temperatures below 240°C the

activation energy was 32.1 kcal/mole, above 240°C there was a non-isothermal decomposition following a power law (activation energy 40.1 kcal/mole). Above 260°C the reaction accelerated rapidly and resulted in a mild explosion. Absorption of ammonia by charcoal was found to be an important factor: it increased the overall rate of decomposition.

Explosive properties

Explosive decomposition of ammonium perchlorate was estimated by Naoúm and Aufschläger [14] to proceed according to the equation:

$$2NH_4ClO_4 \longrightarrow N_2 + 3H_2O + 2HCl + \tfrac{5}{2}O_2 + 266 \text{ kcal/kg} \qquad (3)$$

The volume of gases (V_0) amounts 810 l./kg
the explosion temperature $t = 1200°C$
"force" $f = 4600$ m

The heat of formation $-\Delta H_f$ is 79.7 kcal/mole.

Ammonium perchlorate explodes under the impact of a 10-kg weight dropped from a height of 15 cm. According to Kast [15] the rate of detonation of a sample of density 1.17 g/cm^3, in an iron pipe 35 mm dia. was 2500 m/sec, the net expansion in the lead block being 220 cm^3.

HYDRAZINE PERCHLORATE

Hydrazine perchlorate, $\overset{\oplus}{N_2}H_3\overset{\ominus}{ClO_4}$, m.p. 137–138°C, was obtained by Salvadori [3] from hydrazine and perchloric acid. The substance is as strong an explosive as tetryl, being significantly more sensitive to shock approximating in this regard to mercury fulminate [16].

From aqueous solutions its semihydrate, $(N_2H_5ClO_4)_2 \cdot H_2O$, melting at 85°C is formed. This compound is less sensitive to impact.

FLUORINE PERCHLORATE, ClO_4F

Fluorine perchlorate (b.p. —15.9°C, m.p. —167.5°C) is a gaseous explosive compound prepared for the first time by Fichter and Brunner [17] by the action of fluorine on perchloric acid solution. Rohrback and Cady [18] improved the method of preparing it by using 72% perchloric acid in a platinum vessel.

It possesses properties similar to fluorine nitrate (p. 465). It explodes in contact with organic materials. It is readily decomposed in an alkaline medium:

$$4\,OH^{\ominus} + 2ClO_4F \longrightarrow O_2 + 2ClO_4^{\ominus} + 2F^{\ominus} + 2H_2O \qquad (4)$$

The same reaction can occur with water but the rate of this reaction is low. It possesses strong oxidizing properties.

NITRYL PERCHLORATE (NITRONIUM PERCHLORATE, NITROXYL PERCHLORATE), NO_2ClO_4

This is a crystalline compound which decomposes on heating above 135°C giving off nitrogen dioxide.

Nitryl perchlorate was obtained by Gordon and Spinks [19] by mixing chlorine dioxide with ozone and nitrogen dioxide. Ingold [20] prepared it from nitrogen pentoxide and anhydrous perchloric acid by the reactions:

$$N_2O_5 + 3HClO_4 \longrightarrow 2NO_2^{\oplus} + ClO_4^{\ominus} + H_3O^{\oplus} + ClO_4^{\ominus}$$

$$H_3O^{\oplus} + ClO_4^{\ominus} + 2N_2O_5 \longrightarrow NO_2^{\oplus} + ClO_4^{\ominus} + 3HNO_3$$

Gordon and Spinks [19] also isolated the same product from the precipitate formed by mixing anhydrous nitric and perchloric acid, by fractional crystallization from methanol.

Earlier Hantzsch *et al.* [21] thought the precipitate in question was nitracidium and hydronitracidium perchlorates (p. 13, Vol. I). However Ingold *et al.* [22] showed that Hantzsch's product is a mixture of perchloric acid monohydrate and nitryl perchlorate.

Crystallographic examination [23] and Raman spectra [24] showed that the compound is composed of ions $NO_2^{\oplus}$ and $ClO_4^{\ominus}$. Gillespie [25] found that the following dissociation takes place in sulphuric acid:

$$NO_2ClO_4 + H_2SO_4 \longrightarrow NO_2^{\oplus} + HClO_4 + HSO_4^{\ominus}$$

The compound reacts rapidly with water to yield nitric and perchloric acid. It reacts violently with many organic compounds causing ignition or explosion.

When dissolved in nitromethane it can be used as a nitrating agent.

NITROSYL PERCHLORATE, $NOClO_4$

This is a crystalline compound of density 2.169 g/cm^3, and low stability.

It was first prepared by K. A. Hofmann and Zedtwitz [26] by passing a mixture of nitric oxide and nitrogen dioxide into 72% perchloric acid. The acid was then evaporated to 140°C and on cooling the hydrate of nitrosyl perchlorate $NOClO_4 \cdot H_2O$ crystallized out. The product was dehydrated *in vacuo* over phosphorous pentoxide.

When heated below 100°C it decomposes [27] according to the equation:

$$2NOClO_4 \longrightarrow 2ClO_2 + N_2O_5 + \tfrac{1}{2}O_2$$

At higher temperature the decomposition follows a different course:

$$2NOClO_4 \longrightarrow Cl_2 + N_2O_4 + 3O_2$$

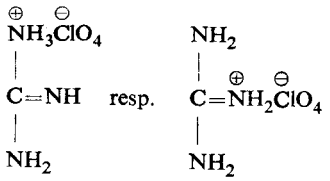
It is a strongly endothermic compound with a heat of formation $-\Delta H_f = 41.79 \pm 0.08$ kcal/mole [27].

It reacts with water with evolution of nitrogen oxides. Ethanol, acetone, dry ether and primary amines react violently with nitrosyl perchlorate causing ignition or explosion.

METHYLAMINE PERCHLORATE

Methylamine perchlorate, $CH_3\overset{\oplus}{N}H_3\overset{\ominus}{Cl}O_4$ (m.p. 210°C) [28], is a substance that resembles cyclonite and PETN in explosive strength. However, it is more sensitive to impact than these compounds.

GUANIDINE PERCHLORATE



(m.p. 250°C)

Marckwald [29] proposed the use of guanidine perchlorate in explosives. It has the important advantages of being stable, non-hygroscopic and moderately sensitive to shock, and is capable of producing a violent explosion. Its preparation, by fusing dicyandiamide with ammonium perchlorate at 150–160°C, offers no significant difficulties.

Guanidine perchlorate heated to a temperature above 300°C undergoes explosive decomposition. Glasner and Makovky [13] studied the thermal decomposition of guanidine perchlorate, and concluded that the decomposition can be expressed by the following equations:

$$CH_5N_3 \cdot HClO_4 \rightleftarrows CN{-}NH_2 + NH_4ClO_4 \quad (5)$$

$$NH_4ClO_4 \rightleftarrows NH_3 + HClO_4 \quad (6)$$

$$3CN \cdot NH_2 \rightleftarrows C_3H_6N_6 \text{ (melamine)} \quad (7)$$

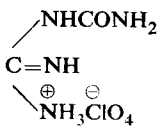
$$C_3H_6N_6 + HClO_4 \text{ (or } NH_4ClO_4) \longrightarrow HCl,\ CO,\ CO_2,\ N_2,\ NH_3,\ O_2,\ H_2O \quad (8)$$

Thus, in the first stage of reaction, ammonium perchlorate and cyanamide are produced. The latter furnishes melamine, which is decomposed in turn under the influence of ammonium perchlorate or the perchloric acid that is produced from the perchlorate.

The activation energy of the decomposition of guanidine perchlorate within the temperature range 390–440°C, quoted in the same contribution, is $E = 30.5$ kcal/mole. The decomposition is catalysed by metallic oxides such as Fe_2O_3, CuO and V_2O_5, and by platinum.

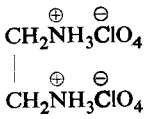
As for its explosive strength, guanidine perchlorate is similar to tetryl. Its sensitiveness to shock is comparable with that of picric acid. The rate of detonation is 6000 m/sec at a density of 1.15 and the net expansion in the lead block test is about 400 cm^3.

DICYANDIAMIDINE PERCHLORATE



Dicyandiamidine perchlorate [30] is an appreciably weaker explosive than guanidine perchlorate, hence it is of no practical importance.

ETHYLENEDIAMINE DIPERCHLORATE



This compound was suggested as an explosive by Stähler [4]. It is a stronger explosive than tetryl, but weaker than PETN. Its disadvantages are high sensitiveness to impact (greater that of PETN) and hygroscopicity. Mainly for this reason ethylenediamine diperchlorate has found no practical application.

According to the Chemisch-Technische Reichsanstalt [31]

the heat of formation $-\Delta H_f$ is	525 cal/g
the heat of detonation $-Q$	900 cal/g
gas volume	842 cm^3/g
expansion in lead block	410 cm^3
rate of detonation at $d = 1.67$ g/cm^3	7150 m/sec

Tetrazene perchlorate is used as an initiating explosive (see Vol. III).

AROMATIC AMINES PERCHLORATES

Spallino [32] has obtained aniline, *p*-nitraniline, *m*- and *p*-phenylenediamine perchlorates, by treating the corresponding amine sulphates with barium perchlorate

TABLE 115

THE PROPERTIES OF AROMATIC AMINES PERCHLORATES (T. URBAŃSKI AND KOWALSKI [34])

Perchlorate of	Melting point °C	Temperature of initiation–explosion within 1 sec at °C	Sensitiveness to shock — 10% of explosions from work of kg	Lead block expansion cm^3	Rate of detonation (glass tube 12 mm dia., density 1.1 g/cm^3) m/sec
Aniline	—	295	1.30	185	5980
o-Nitraniline	206	235	0.40	245	6600
m-Nitraniline	196	245	0.56	235	6825
p-Nitraniline	182	256	0.58	210	6445
m-Phenylenediamine	*	350	1.06	335	—
p-Phenylenediamine	*	326	1.08	235	7825
α-Naphthylamine	*	280	1.48	145	—
β-Naphthylamine	*	290	1.54	45	—
Picric acid (standard)			1.30		

* Melting is almost simultaneous with explosion.

in aqueous solution and evaporating the solution freed from barium sulphate. Lundsgaard [33] suggested using the perchlorates of toluidines, phenylenediamines, and benzidine as explosives.

T. Urbański and Kowalski [34] examined the properties of those perchlorates as well as a range of others, not previously described, to determine their sensitiveness, stability, and explosive strength (Table 115).

Only nitraniline perchlorates are fusible. The others explode without melting.

The investigations carried out by T. Urbański and Kowalski showed that the presence of a nitro group in the aromatic ring of the amine causes the sensitiveness to impact of the salt to increase appreciably, and contributes to its greater explosive strength. The presence of two molecules of perchloric acid combined with phenylenediamine significantly increases the explosive strength, without appreciably increasing the sensitiveness to impact. The initiation temperature of such diperchlorates is higher than that of monoperchlorates, probably as a result of higher melting points.

PERCHLORATES OF HETEROCYCLIC BASES

The very attractive characteristics of the perchlorates of heterocyclic bases were discovered with pyridine perchlorate which was first prepared by Cordier [35] and described by Arndt and Nachtwey [36]. The explosive properties of pyridine perchlorate were described by Muraour and Wohlgemuth [37].

T. Urbański and Kowalski [34] have studied the explosive properties of pyridine perchlorate as well as quinoline and its nitro derivative perchlorates. Due to the introduction of a nitro group the sensitiveness to shock of the quinoline perchlorate increased, but to a smaller extent than the authors had previously observed with primary aromatic amines. The introduced nitro group markedly favoured the increase of explosive strength of the perchlorates (Table 116).

TABLE 116

EXPLOSIVE PROPERTIES OF PERCHLORATES OF HETEROCYCLIC BASES (T. URBAŃSKI AND KOWALSKI [34])

Perchlorate of	Melting point °C	Temperature of initiation–explosion within 1 sec at °C	Sensitiveness to shock — 10% of explosions from work of kg	Lead block expansion cm^3	Rate of detonation (glass tube 12 mm dia., density 1.1 g/cm^3) m/sec
Pyridine	245	335	0.68	245	6650
Quinoline	130	291	0.94	195	—
8-Nitroquinoline	192	303	0.88	240	—
7-Nitroquinoline	172	290	0.84	240	—
6-Nitroquinoline	188	296	0.86	235	—
Picric acid (standard)			1.30		

Hexamethylenetetramine perchlorates (Hexamine perchlorates)

The following salts are known:

perchlorate $(C_6H_2)_6N_3\overset{\oplus}{N}H\overset{\ominus}{Cl}O_4$

diperchlorate $(C_6H_2)_6N_2\overset{\oplus}{(NH)_2}(\overset{\ominus}{ClO_4})_2$

Hexamine diperchlorates are strong explosives. In spite of this the compound has not come into commercial use because of its insufficient stability on storage.

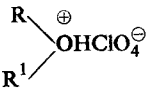
CARBONIUM AND OXONIUM PERCHLORATES

Gomberg in one of his papers on triphenylmethyl (Gomberg and Cone [38]) described carbonium perchlorates, e.g. triphenylcarbonium perchlorate

$$(C_6H_5)_3\overset{\oplus}{C}ClO_4^{\ominus} \text{ (m.p. 150°C)}$$

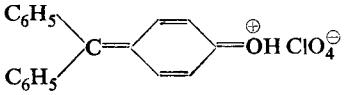
and a number of their derivatives.

Oxonium perchlorates of the general formula



have been obtained by K. A. Hofmann *et al.* and described in a series of papers [39]. They were prepared by acting with concentrated perchloric acid on aldehydes, ketones and ethers. They are extremely unstable crystalline compounds, and all are decomposed immediately by moisture.

Smeets [40] described dioxane perchlorate (m.p. 80–82°C) of the composition $C_4H_8O_2.HClO_4.H_2O$. It was prepared from dioxane and 70% perchloric acid at 0°C. Pfeiffer *et al.* [41] described perchlorates of quinones, e.g. fuchson perchlorate



(m. p. 167°C)

PERCHLORYL COMPOUNDS

Perchloryl fluoride, ClO_3F

Perchloryl fluoride (b.p. -47.5 ± 0.5°C, m.p. -146 ± 2°C) is a gaseous substance prepared for the first time by Bode and Klesper [42] by acting on potassium perchlorate with fluorine at -40 to -20°C. Engelbrecht and Atzwanger prepared the substance by electrolysis of sodium perchlorate in liquid hydrogen fluoride. Barth-Wehrenalp [43] described a new method of preparing it. This consists in heating potassium perchlorate with fluorosulphuric acid (HSO_3F).

It proved to be remarkably stable to high temperature (Engelbrecht and Atzwanger [44]).

It is not hydrolysed by water but reacts quantitatively with NaOH to yield sodium perchlorate and fluoride. It oxidizes iodides to iodine. Perchloryl fluoride reacts with ammonia to yield ammonium perchlorylamide NH_4NHClO_3 [45a]. It reacts with potassium and caesium hydroxide to yield crystalline precipitates of K_2NClO_3 and Cs_2NClO_3. It is isomorphous with metal sulphates, is explosive and very sensitive to flame, shock and friction.

It is quite safe to handle, but being a powerful oxidizing agent, it reacts violently with any oxidizable substance.

Details about the safety in handling perchloryl fluoride are described by Pennsalt Chemicals Corp. [45].

ORGANIC PERCHLORYL COMPOUNDS

This is a new class of compounds recently obtained and described by Inman, Oesterling and Tyczkowski [46]. They are characterized by the presence of the perchloryl group (ClO_3) and their general formula is $RClO_3$. So far only aromatic derivatives of this kind are known.

They are formed by a Friedel–Crafts type of reaction between perchloryl fluoride (ClO_3F) and aromatic compounds:

$$ClO_3F + AlCl_3 \longrightarrow ClO_3^{\oplus} + FAlCl_3^{\ominus}$$

$$C_6H_6 + ClO_3^{\oplus} \longrightarrow C_6H_5ClO_3 + H^{\oplus}$$

$$H^{\oplus} + FAlCl_3^{\ominus} \longrightarrow AlCl_2F + HCl$$

A number of perchloryl compounds were prepared by this method with a good yield.

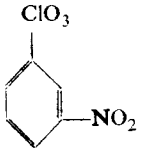
No data on their explosive properties are available, but they are reported to be sensitive to shock and high temperature.

Perchloryl benzene

Perchloryl benzene is a liquid with a b.p. of 232°C and freezing point of −3°C. The density at 30°C is 1.185 g/cm^3.

It can be hydrolysed with potassium hydroxide solution to yield potassium chlorate and phenol. When reduced with hydrogen on palladium it yielded benzene, HCl and water [53].

3-Nitroperchloryl benzene



This was obtained [46] by nitrating perchloryl benzene with a nitrating mixture of anhydrous nitric acid and sulphuric acid. It forms pale yellow needles with a m.p. of 49–50°C.

On reduction with stannous chloride it yielded 3-aminoperchloryl benzene, in the form of colourless needles, m.p. 30–31°C. By acetylation with acetic anhydride and acetic acid it yielded 3-perchlorylacetanilide (m.p. 136–137°C).

4-Fluoroperchloryl benzene

This was prepared by the reaction of fluorobenzene with perchloryl fluoride in presence of aluminium chloride. The compound melts at 28°C and has a b.p. of 53°C (0.25 mm Hg).

2,5-Dimethylperchloryl benzene

This was prepared by perchlorylation of *p*-xylene.

SALTS OF OTHER ACIDS

Among acids capable of forming explosive salts are included those with distinct marked oxidizing properties, e.g. chromic acid, permanganic acid.

Ammonium bichromate, $(NH_4)_2Cr_2O_7$, begins to undergo decomposition at a temperature over 100°C, and explodes at 240°C. Its explosive decomposition proceeds in accordance with the equation:

$$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4H_2O + 310 \text{ kcal/kg} \qquad (9)$$

Initiated with a picric acid detonator, bichromate detonates with difficulty, and within a small space only. It does not take fire from a flame.

Noteworthy properties were discovered in ammonium "trichromate" $(NH_4)_3Cr_3O_{10}$, produced while crystallizing ammonium bichromate from nitric acid, $d = 1.39$ (Siewert [47]). At 190°C the compound undergoes explosive decomposition, evolving nitric oxide and nitrogen dioxide.

The kinetics of the ammonium chromate, bichromate and trichromate decomposition were investigated by Fischbeck and Spingler [48] who measured the increase of pressure with time in an evacuated vessel. The activation energy is 40.0, 49.0 and 34.0 kcal/mole, respectively.

Aliphatic amine chromates, for example methylamine chromate, manifest a more clearly defined explosive character. The properties of hexamethylenetetr-

amine chromate are similar. The aliphatic amine chromates kindle from a flame to burn vigorously.

Ammonium permanganate, NH_4MnO_4, has distinct marked explosive properties, but it is unstable. Decomposition and alteration of the appearance of the compound can be discerned within 1–2 days, and within a few weeks its explosive properties are lost. This is probably due to the decomposition of ammonium permanganate, in accordance with the reaction:

$$2NH_4MnO_4 \longrightarrow NH_4NO_3 + 2H_2O + Mn_2O_3 \quad (10)$$

The temperature of initiation is reported by different authors to be 110–130°C. Bircumshaw and F. M. Taylor [49] have examined the thermal decomposition of ammonium permanganate between 96 and 117°C. The activation energy of this decomposition was estimated as 27.9 kcal/mole. Within the temperature range from 70 to 80°C the energy of activation was 26.0 kcal/mole. An explosive decomposition brought about by an initiator procedes according to the reaction:

$$NH_4MnO_4 \longrightarrow MnO_2 + 2H_2O + 0.5N_2 + 565 \text{ kcal/kg} \quad (11)$$

Ammonium permanganate detonates with a rate of 1700 m/sec. It causes an expansion of 100–125 cm^3 in the lead block test.

Ammonium permanganate is of no practical importance as an explosive. However, its spontaneous formation should be avoided, otherwise an explosion such as one that occurred in a German plant (Roburit Fabrik) at Witten, in 1906, may take place. 0.5% of potassium permanganate was added to an ammonium nitrate explosive, Roburit. Seven hours later self-ignition of the product occurred, followed by an explosion.

Ammonium nitrite, NH_4NO_2. Ammonium nitrite forms deliquescent crystals. On heating it begins to sublime at 32–33°C and decomposes explosively at 60–70°C. It cannot be stored under ordinary conditions as it decomposes at room temperature evolving N_2 and H_2O but the dry salt can be preserved for some time under an atmosphere of hydrogen.

It was prepared by Berzelius as early as 1812 [50] by treating lead nitrite with ammonium sulphate. Later M. Berthelot [50] obtained it by acting with barium nitrite on ammonium sulphate. Erdmann and Sörensen [50] prepared it by acting with dinitrogen tetroxide on coarsely ground ammonium carbonate near 0°C. Ammonium nitrite cannot be obtained from its aqueous solution, as it decomposes on evaporating.

Ammonium nitrite is explosive and very sensitive to heating. Explosive decomposition can occur even when an aqueous solution is heated to 60–70°C. Acidification of an aqueous solution with a drop of concentrated hydrochloric, sulphuric or nitric acid produces a spontaneous decomposition even at room temperature.

Kast [51] examined the explosive properties of ammonium nitrite. He found the heat of explosion to be 803 kcal/kg, temperature of explosion 2210°C, gas volume 1050 l./kg.

The rate of detonation was found to be *ca.* 4000 m/sec at the density of 1.0 and $f = 9865$ m.

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